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American Electrochemical Society

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME [illegible]

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME V.

FIFTH GENERAL MEETING

WASHINGTON, D.C., APRIL 7, 8, 9, 1904

PUBLISHED BY

THE AMERICAN ELECTROCHEMICAL SOCIETY

39 SOUTH TENTH STREET, PHILADELPHIA, PA.

1904

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The publication of this volume has been in the hands of the retiring Publication Committee.

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VOLUME V. 1904

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE FIFTH GENERAL MEETING OF THE SOCIETY, HELD AT WASHINGTON, D. C., APRIL 7, 8, 9, 1904.

(Number of members registered, 52; guests, 38; total, 90.)

SESSION OF APRIL 7TH.

The meeting was called to order at 10 A. M., in the large lecture hall of Columbian University, by President Richards, who introduced Dr. Charles Needham, president of Columbian University. Dr. Needham spoke as follows:

ADDRESS OF PRESIDENT NEEDHAM.

Mr. President and Gentlemen of the Society:

It gives me a profound pleasure to welcome you here this morning, both to the city and to the University. We account it one of the facilities of education that these national scientific societies meet in Washington, and in this University, situated in the heart of the city; it is a part of our educational system.

Washington is the center of things; not because we and our fathers, and grandfathers and great-grandfathers have lived here

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(there are comparatively few people living here who were born in the city of Washington), but, because this is a sort of switchboard, where one can make direct connection with any part of the country; there are representatives here from every State in the Union; there are representatives here from every country on the face of the earth; and at this point you can meet men from every part of the world; the government is carrying on much scientific work, and there are few subjects upon which you can not meet men who have knowledge and information that you are glad to obtain; and because of this centralization of representative and scientific men, I say that Washington is the center of things.

These conditions are very well represented in our own University; our catalogue, issued this month, gives the geographical distribution of our students, and we have students from every State in the Union, only one State having but one representative. We have students from our American colonies, and also from foreign countries. This shows how men gravitate to this city, and how from this place we reach out into every part of the Union with the influence and ideas which are taught or expressed here in educational institutions, and by bodies of men who come to Washington and attend these national meetings.

And so I welcome you here to this center of things, not with any pride of spirit, not with any self-exultation because we are wiser, but because you are wise and you have come here where the influence of your meeting, your education and your knowledge may be distributed over these lines that are radiating over the face of the earth.

I congratulate you, gentlemen, that you are on the front line of educational work, discovering knowledge; that you represent one of the latest—may I say—developments of scientific research and along one of the most important lines for the good of humanity. I congratulate you because along these lines so much is being accomplished that relieves men from much of the drudgery of life; and I account it a spiritual and intellectual benefit to mankind when burdens are lifted from men's shoulders; when we discover that a ton of coal can do more than a hundred men; that there are natural forces that can do the work that has required the hands of men to do; by using these forces we relieve the pressure upon the physical life of man and increase his time and opportunities

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for intellectual and spiritual development. And so you, gentlemen, are on the "skirmish lines," the very outposts of research where ignorance is being driven back, and knowledge of the most useful character is being discovered.

All truth is sacred. The man who discovers the atom and the agencies which break it up is discovering truth that is eternal and sacred; all enlargement of life tends to the saving of men's souls; every fact that results in greater intellectual and spiritual life is quite as sacred as mystical theories about the unknown. I wish we could grasp the thought that all life is eternal and that the higher we can attain in all useful knowledge, the better we can make the conditions of living; the better spiritual and intellectual life we can give to the men and women of this day, the more we live the immortal life.

The man in robes who stands at the altar is no more a true priest, is seeking with no purer heart the truth, than the man who bends over the crucible and the furnace fires trying to discover the truth of matter, the power of matter and the usefulness of things for man.

And so in your life and mine, in whatever field we labor, if we are honestly seeking the truth we are worshiping at the altar of the Eternal.

I welcome you, gentlemen, to this place: to all the opportunities, pleasures and enjoyments of this national city, and if there is anything you want, Mr. President, that you do not see, that we have, please let us know; we shall be only too glad to give it to you. We want to make you as comfortable, and your meeting as successful, as it is possible to be; and in this, let me say, we are not unselfish, because, as I have already said, you are serving us. I thank you. [Applause.]

Response of the chairman, Dr. J. W. Richards:

Mr. President: I wish to thank you, in the name of our society, for your inspiring words, for your hearty welcome and for your hospitality. I know that every member appreciates them: we do feel particularly at home in a university hall, for many of our members are university graduates. The alma maters, the universities of this country, are particularly the home of electrochemical science and industry. I thank you again for your welcome.

After the response of the chairman it was moved and carried

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that a resolution of thanks be offered to the University for its kindness in extending to the society the use of the halls for the purposes of the meeting.

Abstracts of the annual reports of the secretary and treasurer were then read.

On motion of Mr. Carl Hering it was decided to have the reports of the secretary and treasurer printed in full and distributed at the annual meeting, so that their significance could be better appreciated.

The Frenzel Prize of $250, for a thesis on the "Rare Minerals Found in America and their Extraction," as announced a year ago, has not been awarded, there having been no applicants.

The following amendment to the Constitution of the Society, which had been published in due form, was adopted by acclamation:

ARTICLE VI.

Section 2.—The president, vice-presidents and managers shall, after the expiration of the full term of office to which they were elected, be ineligible for immediate re-election to the same office.

Papers by Dr. F. A. Wolf, of the Bureau of Standards, Washington, D. C.; Dr. Henry S. Carhart and George Hulett, of Michigan University, and Mr. W. R. Mott, of Ithaca, N. Y., were read and discussed as printed at length in the Transactions.

EVENING.

At 8 P. M. Dr. Richards delivered the Presidential Address on "The Continuous Advance of Electrochemistry," as printed on page 37 of these proceedings.

SESSION OF APRIL 8TH.

The meeting was called to order at 9 A. M., Vice-President Carhart in the chair during the reading and discussion of the first two papers, followed by President Richards during the remainder of the session.

Papers by Dr. J. W. Richards, Mr. C. J. Reed, Mr. Lawrence Addicks, of the Raritan Copper Works; Mr. Gustaf M. Westmann, of New York (read by Mr. Hering); Dr. Louis A. Par-

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sons, of the University of Utah (read by Mr. Sadtler), and Mr. C. I. Zimmerman, of Wilkinsburg, Pa., and a communicated discussion on the paper of Mr. Lawrence Addicks, by Dr. W. D. Bancroft, were read and discussed, as printed in the Transactions.

Session of April 9th.

The meeting was called to order at 9 A. M. President Richards in the chair.

The tellers of the annual election reported the result of their canvass of the voting for President, three Vice-Presidents, three Managers, Secretary and Treasurer, as follows:

Report of Tellers of Election.

Washington, D. C., April 9, 1904.

To the American Electrochemical Society.

Gentlemen:—We have examined the ballots delivered to us by the Secretary in accordance with the constitution and by-laws, and have the honor to report as follows:

There were 388 votes cast, of which 361 were legal, 17 invalid, and 10 unidentified.

For President, Prof. H. S. Carhart received 191 votes; Carl Hering, 102; Prof. Bancroft, 30; Prof. J. W. Richards, 27; E. G. Acheson and A. H. Cowles, 3 each, and C. A. Doremus, C. M. Hall, L. Kahlenberg, N. S. Keith and C. J. Reed, 1 each.

For Vice-President the votes were—C. J. Reed, 248; E. G. Acheson, 168; Prof. C. F. Burgess, 123; C. M. Hall, 82; A. H. Cowles, 55; S. Sheldon, 44; Carl Hering, 40; C. E. Acker, 38; J. W. Richards, 30; L. Kahlenberg, 28; Dr. C. F. Chandler, 24; C. P. Steinmetz, 22; E. Weston, 14; J. W. Langley, 12; A. E. Kennelly, 11; C. O. Mailloux, 9; H. S. Carhart, 8; W. D. Bancroft, 7; C. S. Bradley, 6; C. A. Doremus, 6; F. M. Becket, W. E. Goldsborough, N. S. Keith, W. H. Walker, 5 each; H. T. Barnes, A. von Isakovics, Thompson (initials unknown), C. P. Townsend, S. P. Sadtler, 4 each; E. A. Sperry, F. J. Tone, W. H. Wahl, 3 each; F. A. J. Fitz Gerald, E. Hart, G. W. Maynard, E. R. Taylor, Thompson (initials unknown), 2 each; D. H. Browne, E. S. Ferry, E. C. Klipstein, A. T. Lincoln, F. J. May-

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wald, J. L. R. Morgan, E. F. Price, E. F. Roeber, P. G. Salom, W. R. Whitney, T. Wolcott, 1 each.

For Manager the votes were—W. H. Walker, 98; C. F. Burgess, 91; C. E. Acker, 84; E. Weston, 79; J. W. Richards, 75; E. G. Acheson, 73; S. Sheldon, 52; H. N. Potter, 49; F. J. Tone, 42; C. J. Reed, 34; D. H. Browne, 32; C. A. Doremus, 32; A. H. Cowles, 30; A. von Isakovics, 26; H. S. Carhart, 24; E. A. Sperry, 23; W. D. Bancroft, 18; L. Kahlenberg, 16; C. P. Townsend, 16; C. F. Chandler, 15; C. M. Hall, 11; H. R. Carveth, 9; F. A. J. Fitz Gerald; 8; N. S. Keith, 7; W. McA. Johnson, 6; Lincoln (initials unknown), 4; R. M. Thompson, 4; C. S. Bradley, 5; W. F. Doerflinger, 5; Messrs. Barnes, O. W. Brown, Carl Hering, W. McA. Johnson, C. P. Steinmetz, P. G. Salom, 3 each; P. T. Austen, W. E. Goldsborough, Loomis (initials unkown), E. F. Price, E. R. Taylor, 2 each; C. Batchelor, E. A. Byrnes, J. W. Langley, J. L. R. Morgan, A. Monell, F. A. Pattison, C. P. Poole, E. F. Roeber, E. E. Ries, H. Rodman, S. P. Sadtler, W. T. Taggart, W. H. Wahl, 1 each.

For Treasurer—P. G. Salom received 265 votes; E. F. Roeber, 30; W. R. Whitney, 18; S. Sadtler, 13; Haskell, 15; Weedon, 1.

For Secretary—S. S. Sadtler received 253 votes; J. W. Richards, 34; A. Isakovics, 26; E. F. Roeber, 23; Carl Hering, 8; W. D. Weaver, 4; W. D. Bancroft, H. S. Carhart and C. J. Reed, 1 each.

Respectfully submitted,

FREDERIC P. DEWEY,
FREDERICK A. HOLTON,
RAYMOND OUTWATER,
Tellers.

The chairman then declared the following candidates elected to hold office for their respective terms: Henry S. Carhart, LL. D., President; C. J. Reed, E. G. Acheson and C. F. Burgess, Vice-Presidents; W. H. Walker, Ph. D., C. E. Acker and E. Weston, Managers; P. G. Salom, Treasurer, and S. S. Sadtler, Secretary.

On motion the report of the tellers was adopted, and a vote of thanks to the tellers for their arduous labors was adopted.

Papers by Dr. Wm. S. Weedon, of the General Electric Co.; Mr. Barry MacNutt, of Lehigh University; Prof. C. F. Burgess,

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of the University of Wisconsin; Mr. W. McA. Johnson, of the Lanyon Zinc Co.; Dr. A. L. Voege, Zurich, Switzerland; C. F. Carrier, Karlsruhe, Germany; E. A. Sjostedt, Sault Ste. Marie, Ont., and Mr. W. H. Davis, Boulder, Colo., and remarks by Mr. S. S. Sadtler on a new construction of porous plate diaphragms, were read and discussed as printed in full in the Transactions.

After the reading of the last paper the meeting adjourned.

PROCEEDINGS OF DIRECTORS

ABSTRACTS FROM THE MINUTES OF THE MEETINGS OF DIRECTORS AND THE EXECUTIVE COMMITTEE, HELD SEPTEMBER 17TH, 1903, TO APRIL 2ND, 1904.

The advisability of establishing Local Sections of the Society was decided upon and the Executive Committee was asked to draw up regulations for their government.

The following regulations, with regard to Local Sections were reported by the Executive Committee and adopted by the Board:

REGULATIONS CONCERNING THE FORMATION AND CONDUCT OF LOCAL SECTIONS.

1. A Local Section of this Society may be authorized by the Board of Directors, at the written request of three members. Only one Section shall be authorized in any one locality.

2. Any member of the Society, in good standing, may enroll as member of any Local Section, provided he complies with the regulations of the said Section. Only members of this Society are eligible to membership in its Local Sections.

3. The regulations of Local Sections are subject to the approval of the Board of Directors.

4. The expenses of each Local Section shall be borne by the members enrolled in said Section. The Society shall not be

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responsible for any debts contracted by a Local Section or the officers thereof.

5. The Society will print advance copies of papers offered to Local Sections, in order to facilitate full discussion thereon, provided that said papers are approved for such advance publication by the chairman of the Local Section and by the Publication Committee of the Society.

6. Papers read before Local Sections, and discussions thereon, if reported, are to be considered as the property of this Society. They shall be submitted to the Publication Committee of the Society and published in the Transactions, if approved by it. Reading of a paper before a Local Section does not carry with it the right of publication in the Transactions.

Papers read before Local Sections may be offered for reading at general meetings of the Society, and will be given equal standing with other papers on the programme of said meeting, when approved by the Committee on Papers.

7. The Board of Directors reserve the right to abrogate, amend or add to these regulations, or to pass upon such questions concerning the welfare of Local Sections not covered by these regulations.

8. Each Local Section shall transmit promptly to the Secretary of the Society, an abstract of its proceedings, including the titles and names of authors of all papers read before it, for the purpose of preparing a report to be published in the Transactions of the Society, and for the purpose of enabling the Board of Directors to comply with Articles III and VII of these regulations.

Permission was granted to establish Local Sections at Madison, Wis., New York City and Philadelphia.

The exchange of Transactions with the Faraday Society was ratified and the arrangement went into execution.

It was agreed with the Faraday Society that our Society pay at the rate of $1.50 per annum for all members entitled to receive the *Electrochemist and Metallurgist* from the Faraday Society in excess of 600, in view of the fact that our membership was so much larger than theirs.

It was decided that members not paying their dues until after the annual meeting would not be entitled to receive the *Electro-*

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chemist and Metallurgist for the year, except upon the payment of $1.50.

Prof. H. M. Goodwin and Mr. Carl Hering were appointed delegates to a Joint Committee of the American Chemical Society, the American Electrochemical Society, the American Institute of Electrical Engineers and other scientific societies, to take under consideration the matter of systematic notation, it being proposed to bring the matter up in September, 1904, at St. Louis.

At a meeting of the Board of Directors, held February 6, 1904, it was decided to fix a salary for the Secretary of $500 per annum, and to allow him $250 per annum for all clerical work, with the exception of the stenographic reports of the proceedings and discussions at the general meetings of the Society. And it was further decided to pay the Secretary's transportation to and from the general meetings, and $5 per day for each day of the general meeting, and for one day preceding the meeting.

Mr. C. J. Reed declined re-election as Secretary.

An invitation from the Committee on Organization of the International Electrical Congress, to co-operate in the proceedings of their Congress, by holding a convention at St. Louis contemporaneously with the Congress, and one or more joint meetings with Section C of the Congress, was received and accepted.

It was decided that but one set of books be kept for the Society, which should be in the hands of the Secretary.

SECRETARY'S ANNUAL REPORT.

APRIL 16, 1903, TO APRIL 7, 1904.

To the Board of Directors of the American Electrochemical Society.

GENTLEMEN:—I submit herewith the following report on the condition of the Society:

Since the last annual report, the Society has held two meetings and the Transactions have been published in Vols. III and IV.

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1,000 copies of Vol. III, bound in cloth, and 1,000 copies of Vol. IV, bound in cloth, and 500 in paper were printed.

260 copies of Vol. IV have been distributed to members of the Faraday Society, in accordance with the arrangement for free exchange of Transactions.

There were on hand December 31, 1903: 401 copies, Vol. I, cloth; 417 copies, Vol. II, cloth; 334 copies, Vol. III, cloth; 355 copies, Vol. IV, cloth; 242 copies, Vol. IV, paper; and on April 5, 1904, there were on hand: 387 copies, Vol. I, cloth; 402 copies, Vol. II, cloth; 296 copies, Vol. III, cloth; 320 copies, Vol. IV, cloth; 240 copies, Vol. IV, paper.

The following data shows the condition of the Society in regard to membership:

Total number of members in April, 1903	492
Number of applicants passed upon since the last annual meeting	186
Number of resignations during the year	16
Number reinstated	1
Number of deaths	2

Respectfully submitted,

C. J. Reed,
Secretary.

TREASURER'S ANNUAL REPORT.

YEAR ENDING DECEMBER 31, 1903.

Philadelphia, April 5, 1904.

To the Board of Directors of the American Electrochemical Society.

Gentlemen:—Herewith I beg to submit my report and condensed balance sheet, as Treasurer of the American Electrochemical Society, for the year ending December 31, 1903:

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ABSTRACT OF TRIAL BALANCE			GAIN	LOSS	ASSETS	LIAB'S
Profit and Loss .	. . . .	$506.94				
Cash	$1275.52	. . . .	. . .	. . . .	$1275.52	
Annual Dues . .	. . . .	3125.00	. . . .	$3125.00		
Initiation Fees .	. . . .	1015.00	. . .	1015.00		
Pub'n Acct . . .	1838.89	. . . .	$1838.89			
Expense Acct. .	1334.61	. . . .	1334.61			
Office Furniture	53.00	. . . .	. . . . .	. . . .	53.00	
Advertising . .	. . . .	179.08	. . . .	179 08		
Frenzel Prize . .	. . . .	250.00	. . . .	. . . .	. . .	$250.00
Due by Members	620.00	. . . .	. . . .	. . . .	620.00	
Dues Prepaid . .	. . . .	46.00	. . . .	. . . .	. .	46.00
	$5122.02	$5122.02	3173.50	4319.08		
BALANCE—GAIN			1145.58			
			$4319 08	$4319.08		
BALANCE—PRESENT WORTH					1948.52	296.00
(as shown by Profit and Loss Account) . . .						1652.52
					$1948.52	$1948.52

PROFIT AND LOSS ACCOUNT.

Credit balance, as shown by balance sheet, December 31, 1902.....	$506.94
Credit balance, as shown by balance sheet, December 31, 1903.....	1,145.58
	$1,652.52

RECEIPTS.

Cash balance December 31, 1902.....	$879,49
From publications	333.09
From advertising	309.26
From initiation fees, 171 members at $5.....	855.00
From dues, 569 members at $5.....	2,845.00
From A. B. Frenzel Prize.....	250.00
	$5,471.84

EXPENDITURES.

For publications	$2,793.96
For expenses	1,349.36
For office furniture.....	53.00
Balance in Fourth St. Nat. Bank, December 31, 1903..	1,275.52
	$5,471.84

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I also append statement of financial condition of the Society to March 31, 1904.

RECEIPTS.

Cash balance December 31, 1903	$1,275.52
From members	2,710.00
From advertisements	74.38
From publications	219.63
From expense	.29
	$4,279.82

EXPENDITURES.

For publications	$145.20
For expenses	361.55
Balance in bank March 31, 1904	3,773.07
	$4,279.82
Cash in bank March 31, 1904	$3,773.07
Cash due from members	1,120.00
	$4,893.07

Examined and approved, Philadelphia, March 31, 1904.

HENRY G. MORRIS,
SAMUEL P. SADTLER.
Auditors.

To this statement to date must be added the value of the inventory of extra copies of Transactions in the hands of the Secretary.

I would also recommend that inasmuch as it is necessary for the Secretary to keep an individual account with each member, that in future the duplication of this work by the Treasurer be abolished, and that merely the amounts received from the Secretary and the cash paid on approved bills be recorded by him.

All of which is respectfully submitted,

PEDRO G. SALOM,
Treasurer.

MEMBERS ELECTED NOVEMBER, 1903, TO MAY, 1904.

November 6, 1903.

M. deK. Thompson, Jr., Boston, Mass.; James N. Gamble, Cincinnati, Ohio; Prof. O. C. Johnson, Ann Arbor, Mich.; Charles A. Catlin, Providence, R. I.; Maximilian Toch, New

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York; J. M. Wills, Akron, Ohio; James Locke, Boston, Mass.; R. E. Fowler, Niagara Falls, N. Y.; C. A. Ernst, Schenectady, N. Y.; George H. Sethman, Denver, Colo.; Arthur C. Hobble, Sivasamudram, S. India; F. W. Huels, Madison, Wis.; Thomas Duncan, La Fayette, Ind.; H. H. Stoek, Scranton, Pa.; Hans Goldschmidt, Essen-Ruhr, Germany; Heinrich Heraeus, Hanau, Germany; M. Namba, Kyoto, Japan; W. T. Burns, Great Falls, Mont.; Herbert Philipp, New York; Frank E. Hanchett, Jamestown, N. Y.; Carlton C. James, Palo Alto, Cal.; N. W. Buch, South Bethlehem, Pa.

December 4th.

H. P. Gibbs, Bangalore, India; Dr. Heinrick Paweck, Vienna, Austria; Gustave Gin, Paris, France; A. T. Smith, Liverpool, England; J. W. Turrentine, Easton, Pa.; F. L. Slocum, Pittsburg, Pa.; Laurent Lowenberg, Cincinnati, Ohio; J. F. Taylor, Cerro de Pasco, Peru; L. J. Lease, Urbana, Ill.; F. J. Pearson, Chicago, Ill.; Whitman Symmes, San Francisco, Cal.; Fausto Morani, Rome, Italy; Ross Phillips, Niagara Falls, N. Y.

January 8th, 1904.

J. T. McNaier, Philadelphia, Pa.; Kenneth B. Quinan, Somerset West, Cape Colony; G. L. Townsend, Washington, D. C.; Henry M. Loomis, Niagara Falls, N. Y.; Orion Brooks, San Francisco, Cal.; Charles A. Marie, Paris, France; Dr. P. L. T. Heroult, La Praz, France; G. Arth, Nancy, France; F. L. Shinn, Madison, Wis.; Ami Gandillon, Geneva, Switzerland; A. Solvay, Brussels, Belgium; Prof. L. A. Herdt, Montreal, Can.; William Stanley, Great Barrington, Mass.; E. J. Prindle, Washington, D. C.; H. M. Fernberger, Niagara Falls, N. Y.; Frederick Conlin, Bethlehem, Pa.; Prof. Wm. L. Dudley, Nashville, Tenn.; Prof. H. P. Talbot, Boston, Mass.; Raymond Outwater, Washington, D. C.; Darragh deLancey, Great Barrington, Mass.; E. R. Barrows, Brandt, Pa.; C. A. Little, Elyria, Ohio.

February 6th.

Archer E. Wheeler, Great Falls, Mont.; Frederick L. Wilder, Minas Geraes, Brazil; H. H. Willard, Ann Arbor, Mich.; Murray

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C. Beebe, Pittsburg, Pa.; Edward Bennett, Pittsburg, Pa.; Frank C. Mathers, Bloomington, Ind.; F. W. MacMahon, London, England; Charles Combes, Paris, France; Dr. Henry Carmichael, Boston, Mass.; Charles H. Dennison, Chelsea, Mass.; Gar A. Roush, Bloomington, Ind.

March 5th.

Earl T. Ragan, Des Moines, Iowa; Dr. Margaret A. Cleaves, New York; Sarat C. Rudra, Calcutta, India; Oliver P. Watts, Madison, Wis.; Edwin A. Zeller, Jr., Philadelphia, Pa.; Clarence M. Kline, Philadelphia, Pa.; Prof. Lucien Ira Blake, Lawrence, Kan.; George McQuilkin, Jr., Quincy, Mass.; Gideon Boericke, Primos, Delaware Co., Pa.

April 2d.

James M. Barrett, Pittsburg, Pa.; John T. Williams, Stamford, Conn.; Dr. Franz Salzer, Philadelphia, Pa.; Adelbert H. Richards, Colorado Springs, Colo.; John D. Pennock, Syracuse, N. Y.; Alexander J. Ewing, Minas Geraes, Brazil; Frederick A. Holton, Washington, D. C.; Henry Gall, Versailles, France; T. B. Stevens, Colorado Springs, Colo.; George A. Hulett, Ann Arbor, Mich.; S. Sakai, Kukura, Buzen, Japan; Prof. Emanuel Paterno, Rome, Italy; George B. Chorpening, Clarksburg, W. Va.; Frederic P. Dewey, Washington, D. C.; Dr. Aug. E. Bonna, Rome, Italy.

April 7th.

Robert P. King, Toronto, Ont., Canada; Addis B. Albro, New York; Ernest Stütz, New York.

May 7th.

Herbert Haas, Redding, Cal.; Clarence I. B. Henning, Santa Cruz, Cal.; Franz von Kügelgen, Holcomb Rock, Va.; F. H. Chapin, Minneapolis, Minn.; H. W. Buck, Niagara Falls, N. Y.; Henry N. Stokes, Washington, D. C.; Dr. Frank A. Wolff, Jr., Washington, D. C.; Henry W. Sykes, Syracuse, N. Y.; Charles Brandeis, Montreal, Canada; Charles H. Clarke, Berlin, N. J.; Horace H. Emrich, Perth Amboy, N. J.

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AMERICAN ELECTROCHEMICAL SOCIETY

DIRECTORY OF MEMBERS

May 7, 1904

[*Members of date April 3, 1902, are charter members.*]

ACHESON, E. G. (Apr. 3, '02) Inter. Acheson Graphite Co., Niagara Falls, N. Y.
ACKER, Chas. E. (Apr. 3, '02) Acker Process Co., Niagara Falls, N. Y.
ACKER, O. E. (Apr. 4, '03) Acker Process Co., Niagara Falls, N. Y.
ADAMS, Prof. C. A. (Apr. 3, '02) Assist. Prof. of Elec. Eng., Harvard University, Residence, 13 Farrar St., Cambridge, Mass.
ADAMS, Ernest K. (Apr. 3, '02) 455 Madison Ave., New York.
ADAMS, Dr. Isaac (Apr. 3, '02) 1776 Massachusetts Ave., Cambridge, Mass.
ADAMSON, G. P. (Dec. 4, '02) Gen. Man., The Baker & Adamson Chem. Co.; res. 233 Reeder St., Easton, Pa.
ADDICKS, Lawrence (Apr. 3, '02) Raritan Copper Works, Perth Amboy, N. J.
AIKEN, Robert H., Consulting Metallurgist, Winthrop Harbor, Ill.
ALBRO, A. B. (Apr. 7, '04) Chemist in Experimental Lab., 82 Morningside Ave., New York.
ALDEN, John (Apr. 3, '02) Pacific Mills, Lawrence; res. Andover, Mass.
ALLEN, Wyatt H. (Sept. 4, '02) Consult. Eng., 331 Pine St., San Francisco, Cal.
ALLYN, R. S. (Feb. 5, '03) Lawyer, 41 Park Row; res. 174 W. 82d St., New York.
AMSTER, N. L. (Apr. 3, '02) Consult. Mining Eng., 32 Equitable Bldg., Boston, Mass.
ANDERSON, E. L. (July 3, '02) Electrochemist, Anderson Elec. Mfg. Co., 119 N. 11th St.; res. 2700 Euclid Ave., St. Louis, Mo.
ARDEN, Henry (Oct. 2, '02) Tesla Coal Co., Stockton, Cal.
ARTH, G. (Jan. 8, '04) Inst. Chimique, rue Grandville 1, a Nancy M. et M. 16, France.
ASKENASY, Dr. Paul (June 6, '03) Jagdstr. 12, Nurnberg, Germany.
ASKEW, C. B. (Apr. 3, '02) Consult. Eng., 1652 Monadnock Bldg., Chicago, Ill.
ATWOOD, Geo. F. (Apr. 3, '02) Western Electric Co., New York.
AUSTEN, Peter T., Ph. D., F. C. S. (Apr. 3, '02) 80 Broad St., New York.
AYLSWORTH, J. W. (Mar. 5, '03) Chem. Eng. and Experimenter, Edison Storage Battery Co., 223 Midland Ave., East Orange, N. J.
BAEKELAND, Dr. Leo (June 6, '03) "Snug Rock," Harmony Park, Yonkers-on-Hudson, N. Y.
BAKEWELL, Thos. W. (Apr. 3, '02) Patent Lawyer, Carnegie Bldg., Pittsburg, Pa.
BANCROFT, Wilder D., Ph.D. (Apr. 3, '02) Cornell University, Ithaca, N. Y.
BANKS, Wm. C. (Apr. 3, '02) Gordon Battery Co., 439-445 E. 144th St., New York.
BARKER, E. R. (Apr. 3, '02) Burgess Sulphite Fibre Co., Berlin, N. H.
BARNES, H. T., Ph.D. (Apr. 3, '02) McGill Univ., Montreal, Canada.
BARNES, S. G. (Apr. 3, '02) Elec. Eng., Solvay Process Co., 310 Boulevard West, Detroit, Mich.
BARR, B. M. (Apr. 3, '02) 234 E. 21st St., Flatbush, L. I.
BARRETT, J. M. (Apr. 2, '04) Vice-Pres. and Treas., Polar Water Co., Center Ave. and Beatty St., Pittsburg, Pa.
BARROWS, Ernest R. (Jan. 8, '04) chemist and mgr. of works, Kessler & Co., Brandt, Pa.
BARSTOW, W. S. (Apr. 3, '02) Consult. Eng., 56-58 Pine St., New York; res. 868 Park Place, Brooklyn, N. Y.
BARTOL, H. W. (Apr. 3, '02) 31, Bd. Victor Hugo, Nice, France.
BARTON, Chas. B. (Sept. 4, '02) Supt. of Electrolytic Bleach Plant, Burgess Sulphite Fibre Co., Berlin, N. H.
BASKERVILLE, Chas., Ph.D. (Apr. 4, '03) Prof. of Chem., Dir. of Laboratory, Univ. of North Carolina, Chapel Hill, N. C.
BATCHELOR, Chas. (Apr. 3, '02) 52 Broadway, New York.
BATES, Wm. S. (Apr. 3, '02) Consult. Eng., 510 Boylston Bldg., Chicago, Ill.
BAUER, Geo. W. (Sept. 4, '03) Vice-Pres. and chem., Bauer-Schweitzer Hop and Malt Co., 1722 Buchanan St., San Francisco, Cal.
BEAL, Prof. J. H. (Sept. 4, '03) Prof. of Chem. and Met., Scio College, Scio, Ohio.
BECKET, Fred. M. (Apr. 3, '02) 170 Buffalo Ave., Niagara Falls, N. Y., Box 158.
BEEBE, M. C. (Feb. 5, '04) Chem., 2210 Farmers' Bank Bldg., Pittsburg, Pa.
BEHREND, Dr. O. F. (Apr. 3, '02) Erie, Pa.
BELL, Alonzo C. (Sept. 4, '03) Manager Bell Elec. Motor Co.; res. 83 E. 116th St., New York.
BENNETT, Edward (Feb. 6, '04) Electrician, Nernst Lamp Co., Amber Club, Pittsburg, Pa.
BENOLIEL, Sol. D., B.S., E.E., A.M. (Sept. 4, '02) Gen. Man. Roberts Chem. Works; res. 14 C St., Niagara Falls, N. Y.

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BERG, Ernst J. (Oct. 2, '02) Elec. Eng., General Elec. Co., Schnectady, N. Y.
BETTS, Anson G. (Apr. 3, '02) care Earl & Wilson, Troy, N. Y.
BIERBAUM, C. H. (Apr. 3, '02) Lumen Bearing Co., 1155 Sycamore St.; res. 312 Prospect Avenue, Buffalo, N. Y.
BIGELOW, S. Lawrence, Ph.D. (May 9, '03) Assist. Prof. of Gen. Chem., Univ. of Michigan; res. 1520 Hill St., Ann Arbor, Mich.
BIJUR, Joseph (Oct. 10, '03) Pres. Electro-Mechanical Co., 29-31 Sullivan St.; res. 310 W. 80th St., New York.
BISHOP, Walter B. (Sept. 4, '02) Assist. Assayer, Granby Smelting, Mining & Power Co., Grand Forks, B. C.
BIXBY, George L. (Aug. 7, '02) 8 Lockwood Ave., E. Cleveland, Ohio.
BLACKMORE, Henry S. (Apr. 3, '02) 206 S. 9th Ave., Mount Vernon, N. Y.
BLAKE, Prof. Lucien Ira (Mar. 5, '04) Prof. of Phys. and Elec. Eng., Univ. of Kansas, Lawrence, Kans.
BLEECKER, John S. (Apr. 3, '02) Seattle Electric Co., Seattle Wash.
BLOCK, Wesley S. (Oct. 2, '02) Pres. Roberts Chemical Co., 40 Wall St., New York.
BOERICKE, Gideon (Mar. 5, '04) Sec. and Treas., Primos Chemical Co., Primos, Delaware County, Pa.; res. Philadelphia, Pa.
BONNA, Dr. Aug. E. (Apr. 2, '04) Societa Italiana di Elettrochimica, Cas post. 214, Rome, Italy.
BOTTINGER, Dr. H. T. (Sept. 4, '02) Pres. of *Deutsche Bunsen Gesellschaft,* Berlin; res. Elberfeld, Germany.
BOGUE, Charles J. (Apr. 3, '02) Mfr. of Elec. Machinery, 213-215 Center St., New York.
BOLLING, Randolph (Apr. 3, '02) Supt. of the Victoria Furnace, The Allegheny Ore and Iron Co., Goshen, Va.
BOON, Prof. John D. (Apr. 3, '02) School of Physic and Chem. John Tarleton College, Stephenville, Tex.
BOWMAN, Walker (Apr. 3, '02) 39 Cortlandt St., New York.
BOYNTON, Dr. C. S. (Apr. 3, '02) Burlington, Vt.
BRADLEY, Chas. S. (Nov. 6, '02) Pres. Atmospheric Products Co., 44 Broad St., New York.
BRADLEY, Walter M. (Apr. 3, '02) Sheffield Scien. School, Chem Laboratory; res. 1346 Chapel St., New Haven, Conn.
BRANDEIS, Charles, (May 7, '04) Consulting Elec. and Mech. Eng., 112 St. James St., Montreal, Quebec, Canada.
BRILL, Geo. M. (July 3, '02) Consult. Eng., 1134 Marquette Bldg.; res. 6510 Yale Ave., Chicago, Ill.
BRINDLEY, Geo. F. (Apr. 3, '02) Niagara Electro-Chem. Co., Niagara Falls, N. Y.
BROCK, Robert C. H. (Apr. 3, '02) 1612 Walnut St., Philadelphia, Pa.
BROOKS, Prof. Morgan (Apr. 3, '02) University of Illinois, Urbana, Ill.
BROOKS, Orion (Jan. 8, '04) Principal Elec. Eng. Dept., Heald's School of Mines and Eng., 130 Union Square Ave.; res. 231 Capp St., San Francisco, Cal.
BROWN, C. D. (Sept. 4, '03) Eng. and Prod. Mgr., Gen. Elec. Co., Windsor, Conn.; res. Hartford, Conn.
BROWN, Harold P. (Apr. 3, '02) Elec. Eng., 120 Liberty St., New York.
BROWN, J. Stanford (Apr. 3, '02) 489 Fifth Ave., New York.
BROWN, Oliver W. (Apr. 3, '02) 430 Francis St., Madison, Wis.
BROWN, W. G., B.S., Ph.D. (Apr. 3, '02) Prof. of Chem., Univ. of Missouri, Columbia, Mo.
BROWNE, David H. (Apr. 3, '02) Chief Chem., Canadian Copper Co., 8 Franklin Ave., New Brighton, S. I.
BROWNE, William Hand, Jr. (Apr. 3, '02) Editor Elect. Review, Park Row Build., New York; res. Wyckoff, N. J.
BUCH, N. W. (Nov. 6, '03) Instr. of Indus. Chem., Lehigh University; res. 117 Church St., Bethlehem, Pa.
BUCHANAN, Leonard B. (Apr. 3, '02) Stone & Webster, 93 Federal St., Boston, Mass.
BUCK, H. W. (May 7, '04) Elec. Eng., Niagara Falls Power Co.; res. 123 Buffalo Ave., Niagara Falls, N. Y.
BURBANK, Prof. J. E. (Apr. 3, '02) Instr. in Physics, Univ. of Maine, Orono, Me.
BURGESS, Prof. C. F. (Apr. 3, '02) University of Wisconsin, Madison, Wis.
BURNS, Willis T. (Nov. 6, '03) in charge of Electrolytic Refinery, Boston and Montana Con. Copper and Silver Mining Co., Great Falls, Mont.
BYRNES, Eugene A., Ph.D. (Apr. 3, '02) Patent Lawyer, 918 F St., N. W.; res. 2539 13th St., Washington, D. C.
CABOT, G. L. (Feb. 5, '03) 82 Water St., Boston; res. 16 Highland St., Cambridge, Mass.
CALDWELL, E. (Apr. 3, '02) 114 Liberty St., New York; res. 50 Westervelt Ave., Plainfield, N. J.
CAMERON, Walter S. (Apr. 3, '02) 239 W. 136th St., New York.
CAPP, J. A. (Sept. 4, '02) Chief of Testing Lab., Gen. Elec. Co., Schnectady, N. Y.
CARHART, H. S., LL.D. (Apr. 3, '02) University of Michigan, Ann Arbor, Mich.
CARMICHAEL, Dr. Henry (Feb. 6, '04) 176 Federal St., Boston; res. Malden, Mass.
CARNAGHAN, E. D. (Apr. 3, '02) Villa Corono, Duranga, Do., Ventanas, Consolidated Mining and Milling Co., Mexico.
CARRIER, C. F. (Mar. 5, '03) Erbprinzenstr. 4, Karlsruhe, Deutschland.
CARVETH, Prof. Hector R. (Apr. 3, '02) Cornell University, Ithaca, N. Y.
CASE, Willard E. (Oct. 2, '02) Auburn, N. Y.

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CATES, Louis S. (Mar. 5, '03) Boston Cons. Copper M. Co., Bingham Canyon, Utah.
CATLIN, Charles A. (Nov. 6, '03) Chem., Rumford Chemical Works, 133 Hope St., Providence, R. I.
CHANDLER, Dr. C. F. (Jan. 8, '03) Prof. of Chem. Columbia Univ., W. 116th St., New York.
CHAPIN, F. H. (May 7, '04) Consulting Eng., North Shore Reduction Co.; res. 2320 S. Irving Ave., Minneapolis, Minn.
CHASTENEY, C. D. (May 9, '03) 74 Cortlandt St., New York; res. Rutherford, N. J.
CHENEY, W. C. (Apr. 3, '02) Elec. Eng., Park Place, Portland, Ore., Box 449.
CHIARAVIGLIO, Ing. Dino. (Apr. 3, '02) Dinamite Nobel Avigliana (Torino), Italy.
CHILDS, D. H. (Apr. 3, '02) Pittsburg Reduction Co., Niagara Falls, N. Y.
CHORPENING, Geo. B. (Apr. 2, '04) 159 Oak St., Clarksburg, W. Va.
CLAPP, E. H. (Sept. 4, '03) Vice-Pres., Penobscot Chem. Fibre Co., 35 Federal St.; res. 490 Beacon St., Boston, Mass.
CLARE, James P. (Apr. 3, '02) Hotel Belleclaire, Broadway and 77th St., New York.
CLARK, Friend E. (Apr. 3, '02) Pa. State College, State College, Pa.
CLARK Wm. J. (Apr. 3, '02) The British Thomson-Houston Co., Ltd., Rugby, Eng.
CLARKE, Charles H. (May 7, '04) Electrochemist, Rodgers & Co., Box 6; res. 123 N. 19th St., Berlin, N. J.
CLEAVES, Dr. Margaret A. (Mar. 5, '04) Physician in active practice, 79 Madison Ave., New York.
COBLENTZ, Virgil, Ph.D. (Apr. 16, '03) Prof. of Chem. and Physics, New York College of Pharmacy, 115 W. 68th St., New York.
COGGESHALL, G. W. (Apr. 3, '02) 620 Atlantic Ave., Boston; res. Chestnut St., Dedham, Mass.
COHO, H. B. (Apr. 3, '02) Contracting Eng., 114 Liberty St., New York.
COIT, Chas. Welles (Apr. 3, '02) International Acheson Graphite Co., 315 Buffalo Ave., Niagara Falls, N. Y.
COIT, Dr. Jas. Milnor (Apr. 3, '02) St. Paul's School, Concord, N. H.
COLBY, Edward A. (Apr. 3, '02) Baker Platinum Works, Newark, N. J.
COLLINS, C. L. 2d (Apr. 3, '02) International Acheson Graphite Co., 315 Buffalo Ave., Niagara Falls, N. Y.
COMBES, Charles (Feb. 5, '04) Eng. of Mines, 29 Ave. Rapp, Paris, France.
CONGER, R. T. (Sept. 4, '03) Chem. Stanley Electric Mfg. Co., Pittsfield, Mass.
CONLIN, Frederick (Jan. 8, '04) Gen. Mgr., The Bethlehem Foundry and Machine Co., 355 Market St., Bethlehem, Pa.
CORNWALL, Prof. Henry B. (June 6, '03) Prof. of Applied Chem. and Min., Princeton University, Princeton, N. J.
CORSON, Wm. R. C. (Sept. 4, '03) Consult. Eng., 440 Capitol Ave., Hartford, Conn.
COWLES, Alfred H. (Apr. 3, '02) 361 The Arcade; res. 656 Prospect St. Cleveland, O.
COWPER-COLES, S. (Oct. 10, '03) Editor "Electrochemist and Metallurgist," Grosvenor Mansions, Victoria St., London, Eng.
COX, G. E. (Apr. 3, '02) Supt. Union Carbide Works, 315 Buffalo Ave., Niagara Falls, N. Y.
CREIGHTON Elmer E. F. (Apr. 3, '02) Stanley Elec. Mfg. Co., Pittsfield, Mass.
CRIDER, J. S. (May 9, '03) Secretary, National Carbon Co., Lock Drawer "L", Cleveland, Ohio.
CROCKER, F. B., Ph.D. (Nov. 6, '02) Prof. of Elec. Eng., Columbia Univ.; res. 14 W. 45th St., New York.
CURTIS, C. C. (Sept. 4, '03) Gen. Mgr. Telephone Co., Sandusky, O.
DARLING, J. D. (Apr. 3, '02) 4826 Greenaway Ave., Philadelphia, Pa.
DAVIES, Meurig Lloyd (Sept. 4, '03) Sec. and Treas., The North American Chem. Co., Bay City, Mich.
DAVIS, D. L. (Aug. 7, '02) Supt., The Salem Elec. Light and Power Co., Salem, O.
DAVIS, F. J. (Mar. 5, '03) Supt. Cowles Elec. Smelt. and Aluminum Co., Lockport, N. Y.
DAVIS, William H. (Sept. 17, '03) Metallurgist and Mill Supt. Idaho Gold Coin M. & M. Co., 1720 Spruce St., Boulder, Colo.
DEEDS, Edward A. (Nov. 6, '02) Asst. Gen. Mgr. National Cash Register Co., Dayton, Ohio.
DE LANCEY, Darragh (Jan. 8, '04) Sec. and Asst. Mgr. Stanley Instru. Co., Great Barrington, Mass.
DE NEUFVILLE, Dr. Richard (Feb. 5, '03) Junghofstrasse 14, Frankfurt a|M, Germany.
DENNIS, Prof. L. M. (Sept. 4, '03) Cornell University, Ithaca, N. Y.
DENNISON, Chas. H. (Feb. 6, '04) Assist. in Testing Lab., The Edison Elec. Ill. Co. of Boston; res. 35 Carmel St., Chelsea, Mass.
DEVINE, Jos. P. (May 9, '03) 313 Mooney-Brisbane Building, Buffalo, N. Y.
DEVLIN, Samuel B. (Jan. 8, '03) Chief Assist. and Dir. of Lab. of Dr. L. Paget, 156 W. 13th St., New York.
DEWEY, Frederic P. (Apr. 2, '04) Assayer to Mint Bureau, Lanier Heights, Washington, D. C.
DICKERSON, E. N. (Mar. 5, '03) Dir. and Couns. Union Carbide Co., Stovall, N. C.
DODGE, Norman (Apr. 3, '02) Elec. Storage Battery Co., 19th St. and Allegheny Ave., Philadelphia, Pa.
DOERFLINGER, William, F., B.S. (July 3, '02) Chief Chem., Acker Process Co., Niagara Falls, N. Y.
DOGGETT, C. S. (Apr. 3, '02) The Grasselli Chem. Co., East Chicago, Ind.

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DONEY, D. C. (Apr. 3, '02) De Lamar Copper Refining Works, Carteret, N. J.; res. Woodbridge, N. J.
DOOLITTLE, C. E. (May 9, '03) Mgr. and Elec. Eng., The Roaring Fork Elec. Light and Power Co., Aspen, Colo.
DOREMUS, Chas. A., M.D., Ph.D. (Apr. 3, '02) 17 Lexington Ave., New York.
DOW, Herbert H. (Apr. 3, '02) Midland, Mich.
DRAKE, Francis E. (June 6, '03) Pres. Lanyon Zinc Co., 607 Carleton Bldg., St. Louis, Mo.
DREYFUS, Dr. Wm. (Dec. 4, '02) Chem. and Mgr., West Disinfecting Co., 162 E. 95th St., New York.
DROBEGG, Dr. Gustave (Jan. 8, '03) Chas. Pfizer & Co., 81 Maiden Lane, New York; res. 100 Dean St., Brooklyn, N. Y.
DRYER, Ervin (Sept. 4, '03) Salesman and Eng., Westinghouse Elec. and Mfg. Co., 171 La Salle St.; res. 26 Ogden Ave., Chicago, Ill.
DUDLEY, Dr. Chas. B. (May 9, '03) Chem., Pa. R. R., Drawer 156, Altoona, Pa.
DUDLEY, Prof. Wm. (Jan. 8, '04) Prof. of Chem., Vanderbilt Univ., Nashville, Tenn.
DUNCAN, Dr. Louis (Sept. 4, '03) Prof of Elec. Eng., Mass. Inst. of Tech., Boston, Mass.
DUNCAN, Thomas (Nov. 6, '03) Vice-Pres. and Gen. Mgr., Duncan Elec. Mfg. Co., 317 S. 6th St., Lafayette, Ind.
DUNN, Clifford E. (Apr. 3, '02) Counsellor-at-Law, 13-21 Park Row, New York.
DURANT, Edward, E.E. (Apr. 3, '02) 115 E. 26th St., New York.
EARL, Wilber T. (Sept. 4, '03) Acker Process Co.; res. 18 Thomas St., Niagara Falls, N. Y.
EASTERBROOKS, F. D. (Apr. 3, '02) Raritan Copper Works, Perth Amboy, N. J.
EDDY, A. H. (Apr. 3, '02) Elec. and Chem., Eddy Elec. Mfg. Co., Windsor, Conn.
EDISON, T. A. (Apr. 4, '03) Orange, N. J.
EDMANDS, I. R. (Aug. 7, '02) Elec. Eng. and Supt. Union Carbide Co., Saulte Ste. Marie, Mich,
EIMER, August (Dec. 4, '02) Eimer & Amend, 205-211 Third Ave., New York.
ELLIOTT, Arthur H. (Apr. 3, '02) Cons. Gas Co., 4 Irving Place, New York.
ELWORTHY, H. S. (Apr. 3, '02) Consult. Chem. Eng., 239 Dashwood House, 9 New Broad St., London, E. C., England.
ELY, Theodore N. (Apr. 3, '02) P. R. R. Co., Chief of Motive-Power, Broad Street Station, Philadelphia, Pa.
EMERY, Arthur L. (Apr. 3, '02) Chem. and Mining Eng., Indiana and 24th Sts., San Francisco, Cal.
EMRICH, Horace H. (May 7, '04) Perth Amboy Plant A. S. & R. Co.; res. 108 Water St., Perth Amboy, N. J.
ENGELHARDT, Dr. Victor (Dec. 4, '02) Chief Chem., Siemens-Halske Co., Vienna III, Stammgasse 12, Austria.
ERNST, C. A. (Nov. 6, '03) Assist. Dir. of Research Lab., General Electric Co., Schnectady, N. Y.
EVANS, Herbert S. (Apr. 3, '02) Instr. in Elec. Eng., Univ. of Neb., Lincoln, Neb.
EVANS, J. W. (Apr. 3, '02) Civil and Mining Eng., Deseronto, Ontario, Can.
EWIN, James L. (Nov. 6, '02) Patent Solicitor, 900 F St., N. W., Washington, D. C.
EWING, Alexander J. (Apr. 2, '04) Elec. Expert, Morro Velho, Minas Geraes, Brazil.
FAHRIG, Ernst (Sept. 4, '03) Tech. Dir., Bauxogen Co., 3642 York Road, Philadelphia, Pa.
FALDING, Fred. J. (Apr. 3, '02) Consult. Eng., 52 Broadway, New York.
FERNBERGER, H. M. (Jan. 8, '04) Chem., Acker Process Co.; res. 618 4th St., Niagara Falls, N. Y.
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Presidential address delivered at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 7, 1904, Vice-President Carhart in the Chair.

THE CONTINUOUS ADVANCE OF ELECTROCHEMISTRY.

By Joseph W. Richards, M.A., A.C., Ph.D.

The field of electrochemical activity covers three distinct lines of endeavor: First, the investigation and classification of electrochemical phenomena—scientific progress; second, the formulation of a satisfactory and all-comprehensive electrochemical theory—intellectual progress; and third, the application of these facts to industrial ends—industrial progress. We purpose to discuss briefly this evening the past achievements in each of these lines of endeavor, in order to determine therefrom and to discuss more at length the present bent and probable future direction and extension of each.

I. The Investigation and Classification of Electrochemical Phenomena.

This is, properly speaking, the real corner-stone of progress in electrochemical science. What has been accomplished in this direction in the century and a half since Beccaria "revivified" several metals by Leyden-jar discharges may be found scattered through the files of our technical journals and compiled from time to time into compendiums of electrochemical literature. The most pretentious, and in many respects the most timely, of all these works is the "ausführliches Handbuch," which our German friends are at present patiently compiling. A careful study of this work causes surprise at both the large amount of investigation which has been done and also at the large gaps which exist in our experimental knowledge. Alongside of splendid researches into the most obscure phenomena of the science exist *lacunæ* in our knowledge of some of the simplest electrochemical phenomena, such as, for instance, in the facts concerning the simultaneous deposition of two or more metals from solution. While doing this

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the impression grows strong upon us that electrochemistry has lost much because of a lack of co-operation among electrochemical investigators, and because of the desultory, haphazard manner in which their efforts have been frequently applied.

The lack of a co-ordinating, directing, systematizing influence among electrochemical workers has been the crying need of the science, and it is just this influence, above all things, which is furnished by our electrochemical societies. The Bunsen Society in Germany, the Faraday Society in England, our own society in America have brought electrochemists together, making them acquainted with each other's work, and in particular with the need of experimental work along neglected lines, and have thus furnished the co-ordinating agency until recently so deplorably lacking.

Davy and Faraday laid broad the experimental foundations of this science by the electrolytic decomposition of many of our most common chemical compounds. Bunsen supplemented this by attacking the rarer metals. Kohlrausch investigated specific conductivities of almost numberless solutions. Beetz and Lorenz fused salts; Moissan the electrochemistry of high temperatures; Hittorf and Ostwald and Nernst the mechanism of electrolysis of solutions, while in between these monumental investigations hundreds of others have contributed to the advance. But still if the army of investigators, as regards numbers, had been in reality an army as regards organization and systematically-directed effort, how much more valuable would its work have been! Is it not a fact that one of the results of our semi-annual meetings is that we learn and have impressed upon us the gaps in experimental electrochemistry, and that we often, either deliberately or tacitly, divide the work among us for systematic investigation?

Let me indicate some of the many electrochemical subjects which need systematic attack and orderly study. The electric conductivity of some common salts are as yet undetermined, not to mention most of the rarer ones. Braun, Graetz and Poincaire did good work on the conductivity of fused salts many years ago, but for every salt they tested there are a dozen or a score awaiting investigation. The results of the electrolysis of solutions of different salts, of different concentrations, at different temperatures, with differing electrodes and current densities, has been merely

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touched here and there, the great body of that information is ripe for harvest to whoever can wield the sickle. The study of the electrolysis of fused salts, or of solutions of chemical compounds dissolved in fused baths, is scarcely begun. One can go into the laboratory any afternoon and start an electrochemical study of a salt which has never before been taken up, and there are enough such to keep the laboratory busy a long, long time.

The use of accurately-controlled electrodeposition for the purpose of determining the chemical equivalents of the metals is a method which has not received the attention which it deserves. It is quite certain that the atomic weights of many elements, whose exact value is at present uncertain, could be fixed satisfactorily in this manner. The calorimetric investigation of electrolytic cells in operation, inaugurated by Faure, is an attractive field wide open for the experimenter, and from which much valuable information could be drawn. Besides these, the deposition of alloys, the solution of alloys, the electrolysis of mixed electrolytes, the functions of intermediate (bi-polar) electrodes, the exact *modus operandi* of porous diaphragms, the relation of viscosity to electric conductivity and ionic mobility, the limitation of the speed of electrolysis by the diffusibility of the products, the solubility of metals in their own fused salts, the function of gases in solution, the compounds of solvent with solute and their relations to complex ions and the mechanism of electrolysis are only some of the many phenomena whose investigation has only begun, and which lie invitingly before us. Prof. A. A. Noyes has blazed a new trail by his systematic work on the electric conductivity of solutions at high temperatures, and Dr. Kahlenberg by his researches on the electrolysis of non-aqueous solutions. Let these advise us that there are as many new fields awaiting attack as there are old ones needing thorough exploration.

In the whole realm of pure science (meaning thereby the investigation and classification of phenomena) there is no field offering more attractions at the present moment, none more ripe for exploitation, none more promising of large rewards for honest work than electrochemistry. The science is yet in its infancy; many of its pioneers are yet living (the original patentee of nickel plating contributes a paper to this very meeting), and the gates of opportunity are opened wide to everyone of us to go and do likewise—to become pioneers in our turn.

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II. The Building of a Comprehensive Electrochemical Theory.

In this respect we must confess at the outset that our science is in a state of transition. We know what we are abandoning, we hardly as yet grasp the newer theory to which we are groping our way. In the past plausible explanations have been advanced which fitted the known facts fairly well, only to be afterwards shattered by new facts which could not be made to fit into the theory. Scientific theories must enlarge to fit the new truth or be broken by it, and so our theories must be in a state of constant flux if the science to which they belong is a live, growing science, receiving continually accretions of new truth.

Not very long ago the burning electrochemical question was, "Is the theory of electrolytic dissociation the true explanation of the nature of a solution?" I shall not say that it is not, because I do not know; but I am certain that the man is making a mistake, whoever he may be, who says that "it is certainly true." My own conception of the state of solution is that the solute is in an abnormal *physical* state, having resemblance to the gaseous state, and that in some cases a definite compound of the solute with the solvent exists in the solution, it also being in the abnormal physical state, but not abnormal chemically. The grounds for this view would take too long to explain, but they appear to me to point to this as an explanation more satisfactory than the assumption of an abnormal chemical condition of dissociation.

Large generalizations like the theory in question, however, are very seldom directly proven false; the evidence of their insufficiency simply accumulates until the conviction arises or grows in men's minds that something else explains the facts better, and the older theory thus fades into the background. At the present time the physical chemist, or perhaps rather the chemical physicist, has thrown so much light upon the structure of the atom by his discoveries regarding electrons that it appears as if a new and a very brilliant side light is about to be thrown upon the subject of electrochemical phenomena. If it be true, as Prof. J. J. Thomson has apparently just proved, that the arrangements of the elements in families according to the periodic law, their periodic increase and decrease in valence and change from electropositive to electronegative character, can be postulated as a necessary deduction from

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the hypothesis of the atoms consisting of uniform shells of positive electricity, inclosing negative electrons arranged in rotating rings, then the ionic conception will of necessity yield place in electrochemical science to the electronic. In this connection it ought to be noted that Professor Thomson's inferences as to what constitutes chemical combination, the electrically neutral atoms losing or gaining electrons and thus becoming positively or negatively electrified, and therefore attracting each other, agree with and supplement to a nicety the system of positive and negative bonds elaborated twenty-five years ago by our respected member, Prof. O. C. Johnson.

The nature of the act of solution bears so fundamentally upon the mechanism of electrolysis that light thrown upon it from any direction is very welcome. Prof. J. H. L. Vogt, of the University of Christiania, has recently published the first section of a work on the nature of fused silicates which bears so directly upon the question of fused baths, and particularly of the condition of compounds dissolved in fused baths, that the close study of his work will undoubtedly assist the electrochemist in understanding fused bath electrolysis and, in fact, the problem of solution in general. It is, indeed, the fact that many bases dissolved in fused silicates retain their chemical individuality, and can be proved to exist there simply in an abnormal physical condition. The analogous process in regard to solution in water passes current under the name of ionization, or electrolytic dissociation. From these and similar investigations the conviction is being pressed upon us that physical solution of one substance in another covers a large part of the field formerly supposed to be entirely chemical in its nature, and that the eutectic mixtures resulting are in no sense chemical compounds, but that the latter constitute nodes or critical points of the mixtures, while in between, in the ordinary run of solutions, we are dealing simply with these chemical compounds mutually dissolved in each other, and in no other states than abnormal *physical* states. The electrolysis of a substance in solution means usually, therefore, the decomposition of that chemical substance existing in an abnormal physical state, and not the act of gathering at the electrodes the ions of the previously dissociated chemical compound.

These are the personal views of your speaker, and are, of

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course, not put forward as necessarily representing those of any other member of this Society. They are given here because I believe that the advance in electrochemical theory in the near future will be in this direction and along these lines.

III. Applications to Industrial Needs.

If electrochemistry concerned itself only with the study of phenomena and their classification, the deduction of laws and the building of theories thereupon, it would satisfy one of the fundamental needs of the human mind, that of *knowing,* but would leave unsatisfied another and equally vital desire, that of *using.*

As one indication of this we see the programme of our meeting classified into experimental, theoretical and industrial. (I stand convicted of having plagiarized the plan of the programme in laying out the subjects of my address.) Without the latter item the electrochemical field would remain a thing apart from the sympathy of the world at large, and it is really by reason of the absorbing interest and great economic value of these industrial applications that we have with us the support and co-operation of the educated and the commercial world.

The various items in which, in industrial chemistry and metallurgy, electrochemical methods have either superseded ordinary non-electric methods, or else have created new industries, form a catalogue sufficiently long to arrest the attention of the most superficial observer, and altogether too long to be mentioned in detail within the limits of this address. Suffice it to mention in passing the millions of dollars' worth of copper electrolytically refined, not annually, but monthly; the 100,000 horse-power consumed in producing calcium carbide; the reduction of the cost of aluminium from $5 a pound to 30 cents; of sodium in almost an identical ratio; the revolution being wrought in one of the largest chemical industries by the production of electrolytic alkali and bleach; the capturing of the potassium chlorate industry and the manufacture of phosphorus.

The whole story, if related at length, would be the old story of *homo sapiens* having discovered a new tool, a new instrument wherewith to torture Mother Nature, a new means of reaching old or of creating new results, and he is necessarily immersed in enthusiasm for this "Genius of the Lamp," which has performed

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so many wonders and promises so many more. For, the use of electricity puts at our disposal temperatures never before industrially attained, gives us a decomposing agent at whose bidding the most powerful chemical compounds resolve into their constituents, enables us to attack and solve chemical problems in a manner before unthought of, opens up a world of possibilities whose scope we even yet but dimly comprehend. This is the fascination of the subject, the attractive force, the absorbing interest which is reflected in the enthusiasm of the electrochemist for his profession and in the gratifying success which has attended the formation and growth of this electrochemical society.

It remains to speak, with as much definiteness as the subject permits, of the possible enlargement and extension of these industrial applications. "Whither" is a more important question than "whence" when the present prosperity and future progress of the art are concerned.

Basing our remarks upon present developments, it may be perceived, to start with, that the electrical methods in chemistry and metallurgy which are most successful are either, *first,* those applied to the more powerful chemical compounds, whose decomposition by non-electric methods is highly difficult and expensive, or else impossible; or, *second,* those applied to new fields of very high temperature reactions impossible of attainment by other means, or, *third,* those applied to ordinary chemical processes, in which the directness of the electrical influence, be it decomposing, reducing or perducing, cannot be duplicated or competed with by known non-electric methods.

Primitive man took his first lesson in metallurgy by learning to make iron; to this the ancients added lead, copper, silver, gold and even the volatile mercury. Many centuries later zinc was distilled, and only in the most recent times have sodium, aluminium and magnesium been possibilities. Painfully and slowly alchemy and modern chemistry toiled up the heights of the electrochemical series, from the easy conquest of the *noble* metals to the powerful mastery of the *strong* metals, and the steepest part of the ascent has been lightened by the aid of electricity, which has in many cases furnished the easy path to the conquest of the most difficult chemical problems.

It is related of our renowned geologist, Clarence King, that he

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was an enthusiastic mountain climber, and having from a distance spied a steep mountain, he conceived the ambition of conquering it. Taking a respite from surveying, he equipped himself for difficult climbing, and after several hours of desperate effort finally stood on the summit of the seemingly impregnable butte, only to find an easy trail leading up on the other side.

The most abundant materials in nature are the fixed, difficultly-transposable compounds of the strong metals, and their conquest and utilization is the peculiar and special province of electrochemistry.

According to the estimate of the indefatigable chemist of the Geological Survey, F. W. Clarke, silicon oxide forms 58.3 per cent. of the contents of the solid crust of the earth, aluminium oxide 14.7 per cent., iron oxide 7.8 per cent., calcium oxide 5.3 per cent. and magnesium oxide 4.5 per cent.; or, expressed in another way, silicon 27.2 per cent., aluminium 7.8 per cent., iron 5.5 per cent., calcium 3.8 per cent. and magnesium 2.7 per cent.

With these figures in mind, may I not ask whether we fully realize the significance of one of the latest electrometallurgical triumphs, the production of metallic silicon on a large scale in the electric furnace by one of our Niagara Falls members, Mr. F. J. Tone? While the catalogues of dealers in rare chemicals are still listing silicon at dollars an ounce, an electrochemist has two barrelfuls of it which he is wondering if anyone will buy at a fraction of a dollar a pound! Could anything better illustrate the revolutionary character of electrochemistry? While the electrochemist is the reverse of a nihilist, we must admit that he is a typical and convicted revolutionist.

To say a word or two more about silicon. I had a somewhat uncanny feeling when Mr. Tone introduced me to his half a ton of silicon. "Here is," I soliloquized, "the first chance which mankind has had to utilize the most abundant solid element on earth. What will be made of it? Can it become as useful as iron? Probably not. Can applications be found for it which will bring it among the ordinary metals of every-day life? Possibly. In any event, here is the material, ready to hand, and no one but the electrochemist could have made it."

Something of the same feeling must have arisen in the mind of the chemist who first made aluminium a commercial possibility,

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but his expectations, based on his chemical process, were only actually realized when the electrochemist gave his solution of the problem. This very element illustrates one of the chief characteristics of electrochemical processes, viz., their potentiality for improvement. Chemically-produced aluminium was out of the race when the metal sold for $1 per pound, yet the present market price is only one-third of that. After the chemical process has done its utmost, has said its last word, the electrochemical process, which supersedes it, has only *begun* its march of improvement.

In the metallurgy of iron, a direct replacement of the ordinary manufacture of pig iron by electrical processes is very far from a possibility, even in countries where coal is most expensive and water power most abundant. However, in the manufacture of that higher-priced product, steel, the case is different, and already some of the finer qualities, such as replace crucible steel, are being made electrically in France, Switzerland and Sweden. It is only a question of some more inevitable improvements being made in the electric furnaces used to make possible the manufacture in them of the more common and cheaper varieties of steel. This will come at first in countries where fuel is dear and power cheap, and afterwards in localities where very cheap power is being generated by gas engines using either the waste gas from blast furnaces or producer gas made from coal waste or culm.

Even before that time the auxiliary use of electric heating to take off the "peak of the load," so to speak, in our open-hearth steel furnaces—that is, to furnish the last few hundred degrees of necessary temperature while the combustion of gas furnishes the lower range—is a distinct commercial possibility. Already our steel works are a network of electrical appliances for running cranes, charging machines, hoists and cars, and the step is not a long one to employ this already-present agent to help the heating gases over the heaviest part of their work, the bringing up of the charge to tapping heat.

Next to iron in natural abundance is calcium, and our chemists and metallurgists are only beginning to appreciate its possibilities. Occurring as almost chemically-pure calcium carbonate, in inexhaustible quantities and at the cost of only a few cents a ton for quarrying, the question of producing the metal cheaply is the particular task of the electrochemist. The cost of the metal is practi-

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cally the cost of its reduction, and there is no doubt that the electrometallurgist can and will solve this question as he has that of aluminium and silicon. Calcium is, at temperatures above a red heat, the strongest metallic base existing, and is therefore the most powerful pyrochemical reagent. By its use many problems may find their solution, such as the complete de-oxidation of melted metals, the reduction of rare elements and many other interesting reactions.

Magnesium does not occur quite so plentifully as calcium, but still it is so common that 99 per cent. of the present cost of making magnesium must be charged against the process used and only 1 per cent. against the raw material. There is no reasonable doubt but that careful study put upon the electrolytic production of magnesium would result in it being produced at a fraction of its present cost. It is certainly a metal which, at its present price, has very limited uses, but, with a specific gravity of only 1.72, a capacity for being hardened and strengthened like aluminium and the property of forming valuable alloys with copper and with aluminium, it is certain that its cheap production would mean another metal added to those in every-day use.

There is yet another metal of kindred character worth considering. Beryllium occurs in the gem beryl as silicate of aluminium and beryllium. The mineral is found massive in large enough quantities to form a commercial source of the metal. The separation of the beryllium oxide from the silica and alumina is not a very difficult chemical operation, but could probably be simplified by the application of Hall's process of differential reduction in the electric furnace. The reduction of beryllium oxide to metal, dissolved in a fused bath of alkaline and beryllium salt is a step which would probably yield to investigation, while the collecting of the metal floating upon the bath should offer no greater difficulties than does the collecting of sodium.

With a brilliant white color, specific gravity 1.6, malleable, ductile, forming fine alloys, there are a large number of possible applications for beryllium if it can be obtained cheaply, and it is to the electrochemist that we must look for the solution of this problem.

In the electrolytic refining of metals copper was the first to yield commercial results, silver next, then gold, lead and bismuth. Yet

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there are others awaiting conquest. The electrolytic refining of nickel, zinc, antimony, iron and tin has been attempted, but not yet commercially mastered; that of aluminum is an attractive question because of the economy it would produce. Instead of purifying by costly chemical methods 4 tons of aluminium ore, we have the alternative problem of refining 1 ton of impure aluminium, and with a large margin of difference in commercial value to work upon. It may be, since electrolysis in aqueous solutions appears impracticable, that refining in non-aqueous solutions, or in easily fusible salts, would conquer the difficulty.

In the field of producing ferro-alloys of the rare metals, for use in making special steels, even the crude electric furnaces in present use have demonstrated their ability to produce these alloys at the minimum cost. Here is a field which has been practically occupied by electric-furnace methods, or by the Goldschmidt process, using electrolytically-produced aluminium, and one does not need to be much of a specialist in chemistry or metallurgy to see the wide vista of commercial opportunities here opening before us.

While our largest electrometallurgical industry is that of copper refining, the largest industrial electrochemical operation is that of producing calcium carbide. Calcium carbide, a substance practically unknown to even the skilled chemist a few years ago, and now being produced by thousands of tons annually. Calcium carbide, the commercial key to the gateway first pointed out by Wöhler, when he made artificial urea.

But why only *calcium* carbide? This is only one of the numerous carbides first produced commercially by electrical methods. Silicon carbide is another which has found broad applications and formed a new industry, and it is not only possible but most probable that other metallic carbides may find large applications. Moissan has shown, for instance, that uranium carbide produces, with water, liquid hydrocarbons, like petroleum, and the production of artificial petroleum is a scientific possibility, although not at present commercially practicable. Besides the carbides, there are other electric-furnace products—the metallic nitrides, which are awaiting further study and utilization.

One of the most vigorous and industrious electrochemists said to me once, "We are so overwhelmed by new things of possible use to science or industry that we can at most investigate only a

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small fraction of them. It is a virgin continent of undeveloped possibilities."

Of the possibilities of the direct preparation of metallic compounds from the metals, the transformation of metallic salts into other compounds, the fixation of the nitrogen of the air, the increased application of the simple, direct and elegant methods of electrolytic decomposition, reduction or perduction in organic chemistry, the electrification of soils and its influence on agriculture, the sterilization of water by electrically-made ozone and the disinfection of sewage and their contribution to sanitary science and the various other unmentioned possibilities of electrochemistry, time literally fails in a simple endeavor to mention, let alone to discuss them.

The great services which electrochemistry has rendered humanity and the march of civilization in the past decades which measure its brief but phenomenal advance, are but a fraction and an earnest of what is yet to be accomplished. If in the battle of industrial competition you are summoned by the conservatives of industry to strike your colors, answer with the courage and determination of the intrepid Captain John Paul Jones, "Surrender! Sir, we have only begun to fight."

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 7, 1904, President Richards in the Chair.

THE STANDARD CELL.

By Dr. Frank A. Wolff, Jr., Bureau of Standards.

Arrangements have recently been completed for holding an International Electrical Congress in connection with the Louisiana Purchase Exposition, by which no doubt some action will be taken in re-defining the fundamental electrical units. It may, therefore, not be out of place to briefly consider the propositions which are likely to be discussed, including a most important point in reference to the preparation of one of the materials—mercurous sulphate—employed in the standard cell.

At the Chicago Congress the fundamental units were defined as follows:

"As a unit of resistance, the international ohm, which is based upon the ohm, equal to 10^9 units of resistance of the C. G. S. system of electromagnetic units, and is represented by the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice 14.4521 grammes in mass, of a constant cross-sectional area and of the length of 106.3 centimeters.

"As a unit of current, the international ampère, which is one-tenth of the unit of current of the C. G. S. system of electromagnetic units, and which is represented sufficiently well for practical use by the unvarying current which, when passed through a solution of nitrate of silver in water, and in accordance with accompanying specifications, deposits silver at the rate of 0.001118 gramme per second.

"As a unit of electromotive force, the international volt, which is the electromotive force that, steadily applied to a conductor whose resistance is one international ohm, will produce a current of one international ampère, and which is represented sufficiently well for practical use by 1,000/1,434 of the electromotive force between the poles or electrodes of the voltaic cell known as Clark's

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cell, at a temperature of 15° C., and prepared in the manner described in the accompanying specification."

The Chamber of Delegates, in which all the leading governments were officially represented, recommended the definitions which they drew up as a basis for international legislative enactment. In looking over the field, however, it is found that comparatively few of the countries have enacted laws defining the fundamental electric units, and that those countries which have are far from being in accord. This naturally suggests that there must be good and sufficient reasons for the lack of uniformity.

In the first place, it is evident that all three of the units should not be concretely defined, connected as they are by the relation known as Ohm's law, and therefore only two are independent and the third should be defined in terms of the other two.

In the second place, the specifications for the silver voltameter were shown to be entirely inadequate.

In the third place, redeterminations of the electromotive force of the Clark cell gave values nearer to 1.433 than 1.434 volts.

In the fourth place, the application of the potentiometer method to measurements of current and electromotive force, and the improvements in the method for measuring low resistances have set a standard of accuracy for relative measurements of the fundamental quantities far in excess of that fixed by the reproducibility of the fundamental standards.

It, therefore, seems that the St. Louis Congress will be called upon to redefine two of the three fundamental units in terms of concrete standards for which the specifications will be much more rigorously drawn, in which case the third unit will be defined in terms of the other two.

The specifications for the unit of resistance are almost free from criticism, and may be made entirely so by the adoption of slight modifications. The unit of resistance will certainly be one of the two fundamental units concretely defined.

For the second one we must, therefore, take either the unit of current, defined in terms of the silver voltameter, or the unit of electromotive force, defined in terms of the standard cell. The arguments in favor of the former were formerly based upon the assumption of Faraday's laws of electrolysis as fundamental laws of nature.

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Although this may be the case, secondary reactions seem to play a not unimportant part where the highest precision is sought. Recent improvements seem to indicate that measurements can be repeated with a given type of voltameter when strictly adhering to certain specifications, to an accuracy of one part in 40,000, which is considerably greater than the accuracy with which, up to this time, the standard cell can be reproduced.

There are, however, a number of objections to the choice of this method of defining the second fundamental unit, viz:

1. With a given silver voltameter, only currents lying within certain narrow limits can be accurately measured.

2. The duration of the measurement must be great enough for the deposition of sufficient silver to permit the weighings to be made with sufficient accuracy.

3. The duration must be great enough to permit the time to be measured with sufficient accuracy.

4. Tedious double weighings must be made to determine the amount of silver deposited.

5. The result finally obtained gives the average value of the current employed, and cannot be utilized for the accurate measurements of other currents except by reference of the result to a standard cell and standard resistance, or to an electrodynamometer, in which case the accuracy is not as great as by a direct reference to the standard cell even in its present state of reproducibility.

Dr. Karl E. Guthe, of the Bureau of Standards, is at present engaged in an investigation of the different forms of silver voltameter which have been proposed, and also some modifications of his own, to determine the conditions under which the most uniform results may be obtained, and the results he has obtained are exceedingly satisfactory. They indicate that the ampère may be defined in terms of the electrochemical equivalent to an accuracy of possibly one part in 40,000.

The points in favor of the choice of the unit of electromotive force as the second fundamental unit, and its definition in terms of the standard cell, may be briefly summarized as follows:

1. The ease with which any voltage may be directly measured in terms of the standard cell by means of the potentiometer with an accuracy practically limited only by the accuracy of its calibra-

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tion and the reproducibility of the cell. This has led to the adoption of the standard cell in Germany as the practical standard of electromotive force, notwithstanding that the ampère is legally defined in that country in terms of the electrochemical equivalent of silver and the volt in terms of the ohm and ampère.

2. The accuracy with which the standard cell can be reproduced, which has for some years exceeded all practical requirements and is still open to greater accuracy by specifying more precisely the manner of purification and preparation of the materials employed, etc.

3. The resulting definition of the ampère in terms of the ohm and volt which corresponds to the actual method employed in precision measurement of current intensity by the potentiometer method. Only a few moments are required for a measurement, and the method is applicable to the measurement of currents of any magnitude, the practical limit being fixed by the carrying capacity of the resistance standard through which the current is sent. The accuracy is limited solely by the errors of calibration of the apparatus employed.

Only the Clark and Weston cells need be considered. In the former, one electrode consists of zinc amalgam in contact with a zinc sulphate solution containing an excess of crystals of zinc sulphate, and the other electrode consists of pure mercury in contact with a paste formed of mercurous sulphate, zinc sulphate crystals and metallic mercury. As the solution which fills the cell is in contact with both the zinc sulphate and mercurous sulphate, it is saturated with both these materials.

The Weston cell differs from the Clark in the substitution of cadmium and cadmium sulphate for the zinc and zinc sulphate.

Investigations thus far recorded indicate that differences between individual cells of either type, set up from materials obtained from various sources agree with each other to within 0.0002 volts, corresponding to a slight advantage in favor of the Clark cell on account of its higher electromotive force.

The constancy of cells of either type is equally satisfactory. Cells set up at different times agree with one another to within the order of accuracy above mentioned if compared a month or more after setting up. The constancy is also attested by the constancy of the ratio between cells of the two types, whether old or newly set up.

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While sharing, equally with the Clark cell, qualities so essential in standard cells, the Weston cell has a number of marked advantages:

1. The high temperature coefficient of the Clark is a serious obstacle to measurements of the highest precision; while that of the Weston cell is at ordinary temperatures less than one-twentieth as large, so that errors due to temperature uncertainties are correspondingly reduced.

2. Another source of error in Clark cells is that due to hysteresis attending temperature variations, which in cells a number of years old may be very considerable. In the Weston cell the equilibrium is more rapidly established and the error can never be as large, owing to the relatively slight influence of temperature on the solubility of the cadmium sulphate.

3. The average life of Clark cells is quite short, owing to the tendency of the cell to crack at the point where the platinum terminal is fused in at the amalgam limb. This objection might be obviated by suitable modifications in the construction as have been suggested, but not without introducing complications. No such tendency has been observed with Weston cells.

4. In Clark cells a layer of gas is formed at the amalgam surface, even when carefully neutralized solutions are employed, which may interrupt the circuit, thus rendering the cell useless. In the Weston cell no gas is formed.

Owing to these marked advantages the Weston cell is certain to displace the Clark cell, and no doubt many advocates of this step will be found among the delegates to the St. Louis International Congress. But, as stated above, the differences between individual cells set up with different materials may far exceed the errors made in current and electromotive force measurements by the potentiometer method, so that it seems desirable to specify more precisely the methods of purification or preparation of the materials employed.

The metals entering into the composition of Clark and Weston cells—mercury, zinc and cadmium—are among the few which can be obtained so pure that no foreign metals can be detected in them by the most refined *chemical* methods. Double distilled mercury answers every requirement, but may contain light metals, which may be eliminated by a preliminary treatment, say, with nitric acid or ferric chloride, or by electrolysis as shown by Jaeger.

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Pure zinc may be obtained from chemically purified zinc sulphate solutions by electrolysis, using platinum electrodes; or if the solution is kept slightly basic, by zinc oxide, using an anode of "chemically pure" zinc of commerce. In the latter case the zinc is deposited in a spongy form, but may be obtained in a more satisfactory form by a subsequent sublimation in vacuo, which also removes any platinum or other heavy metals. By this treatment the impurities are reduced to less than one part in 100,000. The metal may also be obtained by the electrolysis of the fused chloride.

Equally pure cadmium may be obtained by the electrolysis of a cadmium sulphate solution from which the iron has previously been removed by precipitation as ferric oxide, and the lead by electrolysis with small current densities. The metallic cadmium to be purified may be used as the anode and the zinc in the solution remains behind if the current density does not exceed one ampère per square decimeter.

Pure zinc sulphate solution can be obtained by the action of pure sulphuric acid on zinc purified by one of the above methods, a rather expensive process, but this is not an objection where the amount to be prepared is not large. Another method employed by Mylius and Funk, of the Reichsanstalt, is by the action of sulphuric acid on purified zinc oxide obtained by precipitating the latter from a purified ammoniacal solution of zinc sulphate by introducing the same drop by drop into a large volume of water and heating the product thus obtained. The chemically pure zinc sulphate of commerce may, according to the same authors, be purified by precipitating the iron by hydrogen peroxide and zinc oxide and subsequent electrolysis between platinum electrodes with a current density of 0.1 ampère per square decimeter, by which the lead and cadmium are removed. The difficulty of removing the excess of hydrogen peroxide, some of which also seemed to be formed in electrolysis is objectionable, and Dr. H. N. Stokes, of the Bureau of Standards, is working on a method in which the oxidation of the iron is effected by bromine water, the excess of bromine being boiled off and the bromide formed is removed by precipitation with silver sulphate, and the excess of silver can be removed by hydrogen sulphide in the presence of an excess of zinc oxide.

Zinc oxide may be obtained in a high state of purity by the method described above.

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Cadmium sulphate is best prepared in the state of highest purity directly from the pure metal and sulphuric acid; cadmium hydroxide, which is needed in relatively small quantities, can be prepared from the solution of the sulphate by treatment with an alkali, or by a method similar to that for the preparation of zinc oxide.

Fortunately, even considerable quantities of the impurities usually accompanying the above materials exert a relatively small or even insignificant influence on the electromotive force of the cell.

In the Clark cell, the zinc sulphate crystals are easily prepared from the zinc sulphate solution treated successively with zinc oxide and mercurous sulphate, by cooling, owing to the large variation in solubility of that salt with temperature. Cadmium sulphate crystals can be obtained from similarly treated solutions by slow evaporation, or the process can be very much accelerated by evaporating under diminished pressure. Heat must not be applied when mercurous sulphate is present, as the latter decomposes with the formation of a mercuric compound. An equally satisfactory way consists in obtaining the crystals from a carefully neutralized and purified cadmium sulphate solution before treatment with the mercurous sulphate. There is no need of obtaining large crystals; on the contrary, the small crystals are more suitable, as with the latter the equilibrium would be more rapidly established.

The main source of variation of individual cells seems to be in differences in the mercurous sulphate, the remaining ingredient. The "chemically pure" mercurous sulphate of commerce contains, besides nitrates, etc., basic mercurous sulphate, mercuric sulphate, basic mercuric sulphate and possibly sulphites. By washing with dilute sulphuric acid the basic mercurous sulphate is transformed into mercurous sulphate, and the mercuric compounds are removed. The excess of acid may be removed by washing with a carefully neutralized concentrated zinc or cadmium sulphate solution.

The importance of obtaining mercurous sulphate of uniform electromotive properties has suggested the desirability of devising a more direct method for its production in which the materials are the simplest possible and in which the various conditions can be exactly specified.

The relatively slight changes in the electromotive force of Clark and Weston cells, produced by small inverse currents, seem to

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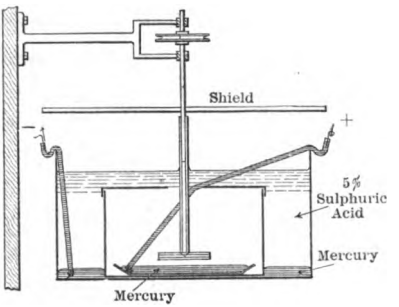
indicate that mercurous sulphate is formed at the mercury electrode under these conditions. An experiment was accordingly made to test this. It was found that with neutral solutions a basic salt containing also mercuric compounds was formed at the mercury anode, while with an acidified solution a beautiful crystalline product was obtained. When the solution is stirred larger current densities may be employed, and in addition there is less tendency for the formation of basic salts due to the accumulation of the product over the surface of the mercury. A most satisfactory product is obtained by the use of a 5 per cent. sulphuric acid solution and a current density of 0.1 ampère per square decimeter. With higher current densities there is a tendency for the mercury surface to oxidize and tarnish, and there is danger of the formation of mercuric sulphate.



The apparatus consists of an outer crystallizing dish containing a second crystallizing dish, of smaller diameter and height, in which is placed a shallow plate having a diameter one or two centimeters less. On the latter is placed pure double distilled mercury which forms the anode, and in the space between the two crystallizing dishes is introduced a layer of mercury forming the cathode. Five per cent. sulphuric acid is then introduced to a depth such that the inner dish is submerged to a number of centimeters. The liquid is stirred by a glass stirrer, driven by a pulley on the shaft of which is also a shield to prevent metal particles from the bearings from falling into the cell. The stirring should be vigorous enough to prevent the whole surface from being covered with the mercurous sulphate formed and to keep the mercury in motion. Connections to the current supply are made by means of glass

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tubes with platinum terminals fused into one end and filled with mercury. To reduce the loss occasioned by the mechanical carrying of the mercurous sulphate out of the inner dish, the latter is covered with a third crystallizing dish, which is inverted and has a hole in its center to permit the introduction of a stirrer and the anode connection. The product formed collects under the rim of the plate and may be subsequently collected.

The sulphuric acid solution contains no trace of mercuric salts, as shown by the precipitation of the dissolved mercurous sulphate with sodium chloride, filtration and treatment with hydrogen sulphide. The mercurous sulphate itself contains no mercuric salt, as shown by a similar treatment.

About five grams of a sample were washed five times with carefully neutralized saturated cadmium sulphate solution and then treated with sodium chloride. The filtrate was neutral, using ethereal iod-eosin as an indicator, showing that there was no excess of acid present, and since the material is obtained from pure mercury and pure sulphuric acid it is hardly likely to contain any other impurities.

It has been suggested that the size of the grain of the mercurous sulphate may have some influence on the electromotive force of the standard cell, which is quite likely the case when the grains are small, owing to differences in solubility. The influence of size of grain on solubility has been shown by Hulett and others for other materials. With the mercurous sulphate produced by the electrolytic method, the crystals are fairly large, as shown by their rapid sedimentation, and there is little likelihood that there will be any difference due to this cause.

Another question which will require settlement in case the volt is defined in terms of the standard cell is the value to be adopted for its electromotive force, and this can hardly be settled satisfactorily until a number of further absolute determinations are made. This is equally true should the ampère be defined in terms of the electro-chemical equivalent of silver.

There are quite a number of other matters which may have an important bearing on the electromotive force of the cell, on which Dr. H. N. Stokes and the writer are at present engaged.

In closing I again wish to emphasize the very marked superiority of the Weston cadmium cell with saturated solution over the

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Clark cell, which should certainly lead to the entire displacement of the latter. I think all who have used cells of both types have come to the same conclusion. The saturated Weston cell should, therefore, be adopted as one of the fundamental standards, if the St. Louis Congress should decide on defining the volt in terms of the standard cell.

As a working standard of electromotive force the portable cell made by the Weston Electrical Instrument Co., in which the solution is saturated at 4° C., and which, therefore, does not contain any excess of cadmium sulphate crystals, can hardly be excelled. A number of such cells have been under constant observation at the Bureau of Standards, and show differences in the course of a year and a half not exceeding a few parts in 100,000. This constancy, together with a temperature coefficient so small that it may be neglected in all but measurements of *extreme* precision, makes it fulfill all the essential requirements of a secondary standard. In addition, the use of such cells simplifies the construction of potentiometers, as no provision has to be made for variations in electromotive force with temperature and the potentiometer current can therefore be adjusted by applying the cell to the terminals of a fixed resistance.

DISCUSSION.

MR. C. J. REED: I understood Dr. Wolff to say that he has an anode of mercury and a cathode of mercury.

DR. F. A. WOLFF: Mercury is employed for both electrodes. The electrolyte is a 5 per cent. solution of sulphuric acid.

MR. REED: Is not the mercury deposited out again on the cathode as fast as it dissolves at the anode?

DR. WOLFF: The mercurous sulphate formed is only slightly soluble and in this manner some is lost by electrolysis, but the loss is not excessive; some of the murcurous sulphate is mechanically carried over to the cathode and is also lost.

MR. REED: Do you get hydrogen at the cathode?

DR. WOLFF: Yes, hydrogen is formed at the cathode and only mercurous sulphate at the anode.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 7, 1904, President Richards in the Chair.

PREPARATION OF MATERIALS FOR STANDARD CELLS AND THEIR CONSTRUCTION.*

By HENRY S. CARHART and GEORGE A. HULETT.

In the preparation of standard cells the chemical side of the problem has hitherto received too little attention. The attempt to obtain more concordant results by giving more attention to the purity of the materials used has led us to investigate the mercurous sulphate, which serves as the depolarizer. The essential results so far obtained will be included in this paper, though the work is not yet completed. We will first describe our method of preparing the other materials.

MERCURY.

The mercury was first shaken with a nitric acid solution of $HgNO_3$, using separating funnels, and was then distilled several times in a vacuum. It is easier to prepare mercury in a high state of purity than the other materials.

CADMIUM SULPHATE.

The chemically pure commercial salt was dissolved at room temperature in its own weight of distilled water with the aid of a motor-driven stirrer. If it was found to be acid to congo red, it was shaken with cadmium oxide, then filtered, and the clear solution was placed in a large crystallizing dish in a room as free from dust as possible. The crystallization is a slow process, but, if carried out as indicated, it will yield perfectly transparent crystals. After about two-thirds of the liquid has evaporated, the mother liquor is poured off and only the clear crystals are taken; those that are white or colored are redissolved, the solution added to the mother liquor, and the whole is then filtered and left to crystallize.

* A preliminary account of an investigation carried out with the aid of a grant from the Elizabeth Thompson Science Fund. The authors desire to express their indebtedness to the Trustees of this fund.

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In working up about 5 kilogrammes of $CdSO_4 8/3H_2O$, the final 100 c.c. of mother liquor contained only the merest trace of zinc; and the zinc, which was the chief impurity to be feared, would be in this last mother liquor, since zinc sulphate is not isomorphous with cadmium sulphate.

The above result indicates that the best chemically pure cadmium sulphate to be had in the market is practically free from zinc.

This method of slow crystallization yields exceptionally clear homogeneous crystals; and these crystals dried on filter paper were used in all our work.

In making a solution of the cadmium sulphate crystals, the difficulty of a very slow rate of solution is encountered. To avoid the formation of another hydrate the solution must not be heated above about 40°. The weighed crystals are brought into an Erlenmeyer flask and covered with three-fourths their weight of distilled water. A Schultz stirrer (Ber. d. d. Chem. Ges., 1896, 2883) is driven by a motor so as to cause the water to circulate just over the crystals for a half day or so, preferably in a bath at 25° controlled by a thermostat. It is best to provide the Schultz stirrer with metal bearings, since glass is liable to abrade. A saturated solution can be made in this way with certainty; some of the crystals will be left and the supernatant solution will be perfectly clear, and will remain so indefinitely. We have found it entirely unnecessary and undesirable to treat the solution as above prepared with cadmium oxide and mercurous sulphate, as has often been advised.

CADMIUM AMALGAM.

A large crystallizing dish is nearly filled with a cadmium sulphate solution, nearly saturated and slightly acid with H_2SO_4. In a small low crystallizing dish is placed a weighed quantity of pure mercury and the whole is immersed in the cadmium sulphate solution, the mercury to serve as the kathode. Connection is made with it by means of a glass-protected platinum wire. The anode consists of pure cadmium, also placed in a small crystallizing dish to catch the dust coming from the disintegration of the cadmuim. The fall of potential from anode to kathode should not exceed 0.3 volt; an ammeter is used to keep a rough account of the quantity of electricity which flows until something more than the

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necessary amount of cadmium has been deposited. The crystallizing dish, with the amalgam and some of the solution, is then removed and is warmed over a water bath till the amalgam melts under the cadmium sulphate solution. When cool it forms a beautiful crystalline button, free from oxide and dust. It may be washed, dried on filter paper, and weighed. The necessary amount of mercury to make a 12.5 per cent. cadmium amalgam may finally be added. It should then be again melted under the cadmium sulphate solution and stirred to insure homogeneity. It will keep indefinitely.

MERCUROUS SULPHATE.

Recently, both in this country and in Europe, variations in the electromotive force of standard cells have been traced to the influence of the mercurous sulphate. But little attention appears to have been given to the problem of working out a standard method of preparing this depolarizer.

Mercurous sulphate can be made by the action of H_2SO_4 on mercury, and the two evidently react at all temperatures and concentrations;* but the reaction is very slow unless the acid is concentrated and the temperature is raised to about 300°. Then the product carries with it sulphuric acid, which is difficult to remove.

Mercurous sulphate, on account of its slight solubility, can be readily prepared by precipitation from aqueous solutions. If we bring together solutions of mercurous nitrate and any sulphate, a white precipitate separates; and if the solutions are dilute and hot, and the one is added to the other slowly, the mercurous sulphate is beautifully crystalline. If this sulphate is washed with water, it turns yellow as soon as the acid has been washed out. Hydrolysis takes place and the resulting solid, according to Gouy (Comptes Rendus, **130**, 1,399), is ($Hg_2OHg_2SO_4H_2O$). This yellow product affects very markedly the electromotive force of the cell, as we shall show later, and its presence is to be avoided.

Gouy found that mercurous sulphate does not turn yellow when washed with an acid solution containing one gramme molecule of H_2SO_4 in 1,000 litres of water. We have found that a more dilute solution does not turn the salt yellow. A concentration of

* Baskerville, Jour. Amer. Chem. Soc., **19**, 874.

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one gramme molecule of H_2SO_4 in 1,900 litres does not change the color of the salt at 25°; while one gramme molecule of H_2SO_4 in 2,000 litres does produce a distinct yellow primrose tint. The higher the temperature, the greater the concentration required to avoid this tint. At ordinary room temperatures the salt may then be washed with one gramme molecule of H_2SO_4 in 2,000 litres. After the mother liquor has been removed by this washing, the process may be completed by washing five or six times with saturated cadmium sulphate solution, exhausting each time by a filter pump. This removes the last trace of acid, leaves the salt moist with saturated cadmium solution and ready to be made into a paste for setting up a cadmium cell. If the mercurous sulphate is to be used in a Clark cell, the final washings will be with concentrated zinc sulphate solution.

Since a small quantity of the salt will make a number of cells, we wash in a Gooch crucible of some 25 c.c. capacity with a tiny filter paper covering the perforated bottom. It is attached to a Bunsen filter flask and a filter pump. By this method the washing can be done in a few minutes. Only about 3 c.c. of the cadmium sulphate or zinc sulphate solution are needed for each of the five or six washings.

Sunlight affects mercurous sulphate, turning it black if the exposure is long enough; and this black product gives in the cadmium cell a decidedly higher electromotive force than the white salt. So the mercurous sulphate which we have prepared by the different methods has been washed with $N/10H_2SO_4$ and has then been kept under the same acid solution in contact with mercury and in a dark room. With these precautions it appears to keep indefinitely.

In order to study the various preparations of mercurous sulphate from the point of view of their use as a depolarizer, we have compared them with one, taken arbitrarily, as a standard. For this comparison we have used a large cell of H-form containing pure mercury in both legs and filled with $N/10H_2SO_4$. The mercury in one leg was covered with the reference mercurous sulphate, and in the other with the particular preparation to be tested. Preliminary experiments showed that when both legs contained the same preparation, the cell had no measurable electromotive force. The experimental concentration cell and a Weston

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cell were kept in a bath at 25°, and the temperature did not vary more than 1/50°. The concentration cell was connected in series with the Weston, and a difference of electromotive force introduced by the concentration cell could easily be measured to 0.000005 volt.

It was easily shown that preparations of mercurous sulphate. made by well-known firms, when tested as above, differed by as much as 1.0 m. v.; and that our own preparations, made by different methods, did not agree. For example, the sample prepared by bringing together $HgNO_3$ and H_2SO_4 gave 0.143 m. v. higher electromotive force than the standard preparation; and that made from $HgNO_3$ and $CdSO_4$ gave 0.206 m. v. In fact, it was found that there was a noticeable difference between two samples of mercurous sulphate made from the same reagents, the only difference in the preparation being that in one A was dropped into B, while in the other B was dropped into A.

These results suggested that perhaps Hg_2SO_4 might carry isomorphously a small quantity of $HgNO_3$, since both of these salts crystallize in similar forms in the monoclinic system, and there is evidence that mercurous nitrate is $Hg_2(NO_3)_2$ in solution. We have been able to detect the nitrate in commercial preparations and in some of those made by ourselves from $HgNO_3$. Tests made by means of the concentration cell show that a trace of $HgNO_3$ added to the standard preparation increases in a marked degree the electromotive force.

The following method has, therefore, been devised to secure Hg_2SO_4 free from the nitrate. We wished to use only mercury and sulphuric acid; to secure at the same time a sufficiently rapid reaction without the use of strong acid, we have employed an electric current. In a flat-bottomed beaker or deep crystallizing dish is placed mercury a centimeter or so deep. This is covered with dilute sulphuric acid (one to six) to the depth of some 10 centimeters. A platinum wire, protected, except at its end, by a glass tube, makes contact with the mercury, which serves as the *anode;* the kathode is a piece of sheet platinum in the H_2SO_4 solution. A current of about 0.3 ampere is passed from the mercury into the solution; crystalline mercurous sulphate at once begins to separate on the surface of the mercury. A stirrer, consisting of a glass rod, bent at right angles at the bottom,

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must be used to keep the mercury surface exposed. The foot of the stirrer passes close to the mercury and must be driven rapidly by a motor.

About 2.8 gm. an hour can be prepared in this way. The sulphate should be protected from the light. By means of a separatory funnel the excess of mercury may be readily removed from below, leaving the sulphate with more or less finely divided mercury mixed with it. The preparation is often somewhat gray on account of the presence of mercury in a state of fine division. This mercury is a distinct advantage, because it insures the absence of the mercuric salt. This method, which is original with one of us and new, so far as we know, gives what we are strongly disposed to recommend as a standard preparation of mercurous sulphate. It gives a lower electromotive force with mercury than any preparation obtained from $HgNO_3$ and H_2SO_4 or a sulphate. Samples made at different times and with different materials show an exceedingly close agreement.

It may not be inadvisable to add the precaution that the sulphate formed during the first few hours should be rejected unless one is sure of the purity of the mercury. After the electrolysis has proceeded for some time, the solubility of the mercurous sulphate is put in evidence by the appearance of mercury on the platinum kathode.

CONSTRUCTION OF THE CADMIUM CELL.

The H-form of cell is the most convenient to fill; and the method, introduced by one of us, of sealing the cell with small blast flames we have made so simple that the two legs may be hermetically sealed at the top without the least danger of affecting the contents of the element.

The glass parts can be readily made by anyone possessing a little skill in glass-blowing. Fig. 1 shows the cell (half the actual size) ready to be filled. The tubing is drawn out and contracted at *a* so as to leave the diameter about 6 mm. and with thin walls at this point. Fragments of the cadmium amalgam may be introduced into the clean dry cell, and may then be melted by dipping the leg of the cell into hot water; or the amalgam may be melted under cadmium sulphate solution, and may then be introduced in the liquid form by means of a small tube, slightly

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contracted at the end, and of a diameter that will allow it to pass freely through the neck *a*. This tube is used as a pipette; it permits the melted amalgam to be introduced rapidly and without splashing. The mercury, the thin paste, and the concentrated cadmium sulphate solution may be introduced in the same manner. An alternative method is to introduce the materials through little funnels made out of small test tubes. The funnels must pass through the neck *a* of the cell and must reach well down toward the bottom.

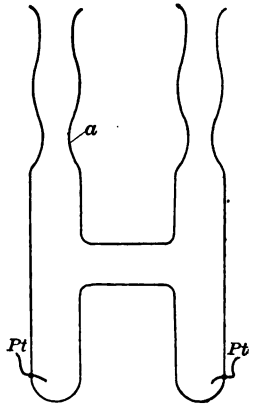

FIG. 1.

The electrolytic mercurous sulphate, which has stood with mercury under dilute sulphuric acid, is brought into a Gooch crucible, avoiding free mercury, which interferes with the filtering; it is then washed first with sulphuric acid (made by adding 0.5 c.c. concentrated H_2SO_4, density 1.84, to a litre of water), and then with concentrated cadmium sulphate solution, as described above. It is better to reject the top layer, which may be slightly darkened. The paste is next made in a a clean agate mortar by grinding together crystals of $CdSO_48/3H_2O$, and a little mercury, and then mixing in about three volumes of the mercurous sulphate and enough saturated cadmium sulphate solution to make a thin paste. After the mercury and the paste have been introduced into the positive side of the cell, both legs are filled up to the cross tube with the dry clean crystals of $CdSO_48/3H_2O$. Enough of the saturated cadmium sulphate solution is finally added to fill the cell to the top of the cross tube. The sealing-off is readily done

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TABLE OF RESULTS FOR CADMIUM CELLS

Date		Jan. 6, 1904	Jan. 8, 1904	Jan. 11, 1904	Jan. 19, 1904	Feb. 1, 1904	Feb 15, 1904	Feb. 16, 1904	Feb. 17, 1904	Feb. 18, 1904	Feb. 20, 1904	Feb. 22, 1904	Feb. 24, 1904	Feb. 25, 1904	Feb. 27, 1904
Temp.		21.1°	21.1°	21.1°	21.1°	21.1°	21.1°	21.1°	21.1°	21.1°	21.1°	21.2°	21.1°	21.0°	21.0°
B 1	Jan. 28, '03	1.01936$_5$	1.01935+	1.01937	1,01936	1.01936$_5$	....	....	....	....	....	....	....	....	1.01936$_5$
B 2	Mar. 9, "	29	27	28	28	27	....	....	....	....	....	....	....	....	27$_5$
B 3	" " "	31	30	30$_5$	31	29$_5$	....	....	....	....	....	....	....	....	30
B 4	" " "	29	28	28	29	28	....	....	....	....	....	....	....	....	28
B 5	" " "	31	30	30	30	30	....	....	....	....	....	....	....	....	29$_5$
B 6	June 22, "	36	35$_5$	34	35	35	....	....	....	....	....	....	....	....	34$_5$
B 7	" " "	36	36	36	36	36	1.01936	1.01036	1.01936	1.01936	1.01936	1.01936	1.01936	1.01936	1.01936
B 8	" " "	35$_5$	36	35	35	35	....	....	....	....	....	....	....	....	34$_5$
B 9	" " "	33	34	33	33$_5$	33	....	....	....	....	....	....	....	....	33
B10	" " "	35	35$_5$	35	35	35$_5$	....	....	....	....	....	....	....	....	36
D 1	Dec. 21, "	08	07	06+	06	06$_5$	07$_5$	07	07	07	....	07	....	07	07
D 2	" " "	09	07+	07	06$_5$	06$_5$	08	07	08	08	....	08+	....	08+	08
D 3	" " "	09	08	07	07	07	08	08	08	08	....	09	....	08$_5$	08
D 4	" " "	09	08	08	97+	07$_5$	09	08	08+	08+	....	09	....	09	08
D 5	" 24, "	63$_5$	50	44	37$_5$	35	....	....	....	....	....	....	....	....	31$_5$
D 6	" " "	64	48	42	36	33+	....	....	....	....	....	....	....	....	29
D 7	" " "	54	45	41	36	34	....	....	....	....	....	....	....	....	30
D 8	" " "	58$_5$	46	42	35	31	....	....	....	....	....	....	....	....	27
D 9	" " "	61	49	44	37	33	....	....	....	....	....	....	....	....	29
D10	" " "	68	53	47	39	34	....	....	....	....	....	....	....	....	29
F 1	Feb. 15, '04	....	....	....	....	....	07	06$_5$	07	07	07	07$_5$	08	08	07$_5$
F 2	" " "	....	....	....	....	....	07	06	07	07	07+	08	08+	08	07$_5$
F 3	" " "	....	....	....	....	....	07	07	07	07	07$_5$	08	08+	08	07$_5$
F 4	" " "	....	....	....	....	....	08	08	07+	07	08	08	08$_5$	08	07$_5$
F 5	" " "	....	....	....	....	....	08	07	07	06	08	08	08$_5$	08$_5$	08
F 6	" " "	....	....	....	....	....	06$_5$	06	06	07	08	08	09	08$_5$	08
F 7	" " "	....	....	....	....	....	07	06	07$_5$	07	07$_5$	08	08	08	08+
F 8	" " "	....	....	....	....	....	08	07	07$_5$	07$_5$	07	08	08+	08	08
F 9	" " "	....	....	....	....	....	05	07	07	07	08	08	09	09	08$_5$
F10	" " "	....	....	....	....	....	07	06$_5$	07	07	07$_5$	08	08	08	08+
G 1	Feb. 15, '04	....	....	....	....	....	21$_5$	18	18$_5$	17	17	15	17—	16$_5$	15$_5$
G 2	" " "	....	....	....	....	....	1.02022	1.02000	98	94$_5$	92	90	87—	86	83
G 3	" " "	....	....	....	....	....	1915	1911	11	12	12$_5$	11	12—	12	11$_5$
G 4	" 20, "	....	....	....	....	....	....	....	....	....	1.02028	1.02008	1.02002	1.02001	98
G 5	" " "	....	....	....	....	....	....	....	....	....	26	14	10	08+	1.01015+
G 6	" " "	....	....	....	....	....	....	....	....	....	31	21	12	03	11

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by means of two small horizontal blast flames, 3 cm. long, directed in a line toward each other and just meeting. The narrow part *a* of the cell is brought between the impinging flames, the glass quickly softens, and the top part is drawn off. There is no noticeable heating of the contents of the cell; but it may be advisable, before one has acquired the proper skill, to protect the cell by an asbestos disk fitted to the tube below the point *a*. The disk is not necessary if the cell is made like the one shown in Fig. 1. A cell sealed in this way contains nothing except the materials of the voltaic combination. It cannot leak and can be immersed in kerosene without danger of the oil getting inside. A perfect seal has always been a most difficult thing to secure.

All the cells above tabulated were filled and sealed as described. The dates on which they were set up are contained in the second column; they are numbered in groups of 10, because they are mounted in racks holding 10 cells each for convenience in placing them in a large 60-litre kerosene oil bath. The temperature of the bath was automatically regulated and the oil was thoroughly stirred by a motor-driven stirrer; the variation of temperature was not more than one-tenth of a degree at any time. It remained practically constant for days at a time.

The cells were compared by means of a Feussner direct-reading potentiometer, made by Otto Wolff, of Berlin. The comparisons can be made rapidly and with certainty to the fifth decimal place.

It will be noticed that B1 to B10 are relatively old cells that had settled down to a constant value; they were assumed not to vary more than 0.00001 volt when kept at a fixed temperature. B7 was taken each time for setting the potentiometer at 1.01936, which is the electromotive force obtained for the cadmium cell at 21.1° by assuming the Clark at 15° as 1.434 international volts, and the ratio of Clark at 15° to cadmium at 20° as 1.40670.* These cells, B1 to B10, were set up in accordance with the most approved information available at the time, and they must agree closely with the cells used for determining the Clark 15 degrees cadmium 20 degrees ratio of 1.40670.

D1 to D4 were the first cells made in which the electrolytic mercurous sulphate was used. They were put up December 22, 1903; and, while they were not put into the constant temperature

* Zeitschrift für Instrumentenkunde, February, 1901.

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bath till January 5, 1904; they showed from the first a large and constant difference from B7. Previous to January 6th their value relative to B7 had not changed perceptibly; the table shows their behavior since January 6th. These cells do not appear to have changed since they were set up by more than one part in a 100,000, and the agreement among themselves is exceptionally good. Their electromotive force is about 28 parts in 100,000 lower than B6 to B10.

The next series made with the electrolytic mercurous sulphate were set up February 15, 1904. The materials used were different from those used in the construction of D1 to D4, but they were prepared as already described. The cells composing the F series were put into the bath and compared within six hours after they were set up. The table shows their history for the first twelve days. The very small variations which they exhibit may be more apparent than real, because they may be due in part, at least, to small variations in the reference cell B7.

It will be noticed that the cells of this F series are identical with D1 to D4, and that their apparent electromotive force is 1.01908 international volts at 21.1°.

Cells D5 to D10 were made with mercuous sulphate prepared by adding a solution of mercurous nitrate to a cadmium sulphate solution; it was the same sample which gave in our test cell an electromotive force 0.206 m. v. greater than the standard electrolytic preparation.

When these cells were first compared, immediately after setting up, they were markedly higher than B7, but their electromotive force fell rather rapidly at first, and very uniformly after they were placed in the constant temperature bath. The table shows their history from January 6th; the upper curve in Fig. 2 was plotted from the data pertaining to D6 from January 5th for the first nine days after its temperature was maintained constant. The contrast between the behavior of this cell and that of D1, which is shown graphically in the lower curve of Fig. 2, is very marked and very characteristic. Professors Jaeger and Lindeck called attention some time ago to the rapid fall in electromotive force shown by some cadmium cells set up with mercurous sulphate obtained from one, at least, of the best manufacturers.* We

* Zeitschrift für Instrumentenkunde, Feb., 1901.

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consider it an accomplishment of considerable value and interest to be able to make cells that do not require the ageing process to reach their equilibrium in electromotive force. The electrolytic method of preparation furnishes us with a mercurous sulphate absolutely free from any nitrate, and with cells that reach their equilibrium immediately. This fact, together with the lower value of the electromotive force, compared with that of cells made by the use of mercurous sulphate prepared in any other way, points to the purity of the electrolytic salt, compared especially with that made from the nitrate of mercury.

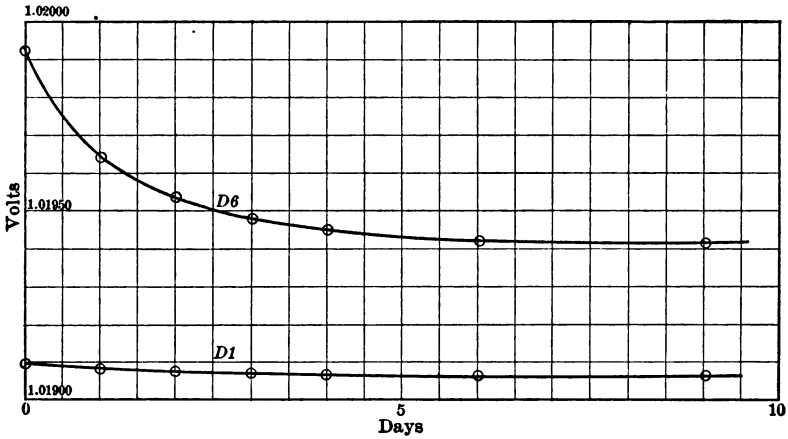

FIG. 2.

The cell marked G1 was set up with electrolytic sulphate of mercury, to which a trace of mercurous nitrate was added and mechanically mixed in the paste. G1 shows both the time element and the higher electromotive force.

Cell G2 was made with mercurous sulphate which had been exposed to sunlight for six weeks (under $N/10H_2SO_4$) and which was quite black. The cell has a very high electromotive force, showing that the salt discolored by sunlight has undergone a marked change and needs further investigation. After a cell has been set up the discoloration produced by the light is probably only superficial and may not affect the electromotive force seriously; but it is better to avoid the discoloration by excluding the light from the cell.

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The mercurous salt used in G3 was made from recrystallized *mercuric* sulphate ($HgSO_4$), which was shaken with mercury in dilute sulphuric acid. The reduction is brought about by vigorous shaking so as to insure the fine division of the mercury and its distribution throughout the salt. The electromotive force of this cell is very close to those made with the electrolytic sulphate; the slight time element indicates a slight impurity. This experience indicates also that the high electromotive force of other cells is not due to the presence of the mercuric salt.

Cells G4, G5, and G6 were made with mercurous sulphate which had been turned yellow by shaking with water and mercury, renewing the water six times, or until the conductivity of the solution was constant, showing that no further change was taking place. These cells have also a high electromotive force, and the mercurous sulphate modified in this way presents another problem to be worked out. Indeed, this preliminary work has opened up a large field for chemical investigation, which we hope to report on later.

This paper deals with cadmium cells only. We have made fifteen Clark cells with the electrolytic mercurous sulphate. They show excellent agreement, but we are not yet ready to report on them.

DISCUSSION.

MR. A. N. POTTER: I would like to ask whether there is any standard as to the containing vessel—the glass. Glass is in general a very poorly-defined material and somewhat soluble. We now have silica and special glasses that are better defined, and it might be well to carefully specify the container, both as to material and preparation.

DR. H. S. CARHART: We have used the same kind of glass, I think, throughout. I am not sure that those I made first are just the same as are those that were made in the chemical laboratory; but I think it is all German glass. We have kept that element practically constant, so far.

MR. POTTER: Glass would be one of the things most likely to vary from country to country and from place to place; and any one who has had experience in evacuating glass vessels of various kinds of glass, made by different glassblowers, is aware that the character of the glass and the condition of its inner surface after

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blowing is not a negligible factor, where the highest uniformity is required.

PRESIDENT RICHARDS: I would like to ask Professor Carhart whether the temperature which has been measured—has been given in centigrade degrees as determined by the mercury thermometer; or whether he has or not transformed them into absolute temperature as given by an air thermometer; because, in getting to such accuracy—one part in one hundred thousand—it would make considerable difference.

DR. CARHART: I failed to call attention to one thing: we have used mercury thermometers, and latterly all the time a thermometer reading to hundredths, which has a Reichsanstalt certificate with it; but so far as these cells are concerned, such extreme accuracy in temperature is not necessary. The total variation for one degree centigrade for a cadmium cell is a little less than four-tenths of one of these large divisions in the diagram. If the reading was a tenth of a degree off (and there is no excuse for its being off more than that), we would have only four-tenths of one-tenth of one of these divisions here, which is only half of one in the fifth decimal place; and no one wants to measure as accurately as that. There is no object in it. It is not necessary with the cadmium cells to know the temperature as accurately as with the Clark cells.

DR. F. A. WOLFF: It is rather interesting to learn of the properties of this electrolytic mercurous sulphate. So far I have not had the time or opportunity of setting up any cells with this material; but I have felt very confident, from its crystalline character and from its freedom from all impurities, that it would give satisfactory results. I have in this tube a sample of the material which I have obtained, and which shows its crystalline character very nicely by turning the tube. (Exhibits tube).

DR. CARHART: I want to call attention to one thing on which, I think, a question was asked. If we adopt the cadmium cell, as I thoroughly believe we ought to, we should call it, perhaps, the Weston primary cell when it contains crystals of cadmium sulphate, that is, a primary standard. The other one that the Weston Co. makes is a secondary standard for commercial purposes. We have other primary standards. We do not use those for practical commercial work. We have also secondary standards that we use for commercial measurements. It is these primary stand-

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ards that we use for extreme accuracy, that perhaps ought to be called the "Weston primary cell;" the other, the "Weston secondary cell." There is some confusion now. Unless we specify by a descriptive phrase, we do not know which is meant.

MR. CARL HERING: I would like to ask whether there is not some uncertainty introduced in hermetically sealing the cells? Quite a number of years ago, before we knew as much as we do now about standard cells, I was experimenting with a Daniel cell and found that quite perceptible variations were produced by very slight differences of pressure in the cell itself, like the pressures produced by the two columns of the two liquids. Slight differences in pressure due to inserting the cork more tightly on one side produced quite appreciable differences in the electromotive force. It seems to me that similar uncertainties might be introduced by sealing off the Clarke and Weston cells, because the internal pressures would necessarily be different in different cells.

DR. CARHART: In the first place, I would like to direct Mr. Hering's attention to these series of numbers. If there is very great difference in the pressure, and if that makes much difference in the electromotive force of the cell, we ought to have more difference than these show. In the second place, I think your variations came from difference of pressure in the two limbs. We have no difference of pressure in the two limbs; there is the same pressure in the two sides, and the pressure inside is not different from that outside materially; for when the glass is soft, if there is excess of pressure outside over inside, the glass would subside. The excess of pressure over atmospheric pressure is very small.

MR. C. J. REED: About what temperature is the material in the cell?

DR. CARHART: Near 20 degrees, usually, in the laboratory.

MR. REED: The probability is that the pressure inside, at almost all ordinary temperatures, would be the same as atmospheric pressure.

DR. CARHART: I think so.

MR. REED: Probably a little less.

DR. CARHART: No essential difference.

PRESIDENT RICHARDS: The pressure would be, I think, considerably less than atmospheric, because in sealing the air inside is heated; and therefore as it cools down afterwards it becomes less than atmospheric pressure.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 8, 1904, Vice-President Carhart in the Chair.

SINGLE POTENTIALS OF THE HALOGEN ELEMENTS.

By William Roy Mott.

There are many points in the ionization theory not in harmony with some facts observed in the study of single potentials. The *impossible*[1,2,3] solution tensions assigned to metals tend to blind one to the fact that the *actual chemical reaction*[4] taking place and its free and bound energy are the essential points.

Dr. Patten and the author[5] have calculated the single potential of chlorine for *dilute aqueous* solution as —2.00 volts. By similar methods, the author has calculated the single potentials of the other halogen elements; iodine, —0.87 volt; bromine, —1.53 volt; fluorine, —2.53 volts, which values will be used in the reverse process of calculating the single potentials of metals.

In Table I, Column I contains the metals; Column II, the experimental values of the single potentials of the metals against their chlorides. All the single potentials, given in this paper, are referred to Ostwald's zero[6]. These experimental values are Neumann's[7], except those given for the alkali metals[8]. The rest of the table consists of calculated decomposition voltages (D. V.) and calculated single potentials (S. P.) for dilute[9] aqueous solu-

[1] The enormous magnitude of the solution tensions given to metals have been shown by Lehfeldt (Phil. Mag. [5] Vol. 48, 1899) to be incompatible with molecular physics.

[2] Kahlenberg has pointed out the important relation between heat of solution and single potential. See Jour. Phys. Chem., 1899, p. 379

[3] Compare F. Krüger Zeit. Phy. Chem., 1900, Vol. 35, p. 19.
Lehfeldt Zeit. Phy. Chem., 1900, Vol. 35, p. 257.

[4] The single potential observed with aluminum and magnesium is not that due to the formation of *normal* salts but of *basic* salts. It is well known that these metals dissolve in solutions of their own salts. See
Lemoine, Comptes Rend., 1899, **129**, p. 291.
Kahlenberg, Jour. Amer. Chem. Soc., 1903, **25**: 380.
C. F. Roberts and L. Brown, Jour. Amer. Chem. Soc., 1903, **25**: 801.

[5] Electrochemical Industry, September. 1903, I: 450.

[6] Normal calomel electrode is taken as—0,56 volts. See Carveth, Jour. Phys. Chem., 1898, **2**: 289.

[7] Zeit. Phys. Chem. 1894, **14**: 229.

[8] Patten and Mott, Electrochemical Industry, September, 1903, and Jour. Phys. Chem., 1904.

[9] "Dilute" in thermal chemistry usually means normal to tenth normal.

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tions. The original thermal data used is that given in Reychlor's "Outlines of Physical Chemistry." The calculated decomposition voltages do not include factors due to entropy, as the temperature co-efficients are practically unknown. The single potential of the metal is obtained by subtracting the single potential of the halogen from the total voltage.

TABLE I.

DECOMPOSITION VOLTAGES.

Col. I.	Col. II.	Fluorides.		Chlorides.		Bromides.		Iodides.	
Metal.	Exp. Values	D. V.	S. P.	D. V.	S. P.	D. V.	S. P.	D. V.	S. P.
K^{I}	+2.38	4.98	+2.41	4.38	+2.38	3.93	+2.40	3.26	+2.40
Na^{I}	+2.18	4.80	+2.23	4.18	+2.18	3.73	+2.20	3.06	+2.20
Li^{I}	+2.45	5.04	+2.47	4.44	+2.44	3.98	+2.45	3.31	+2.45
Ca^{II}				4.08	+2.08	3.60	+2.07	2.93	+2.07
Sr^{II}				4.26	+2.26	3.78	+2.25	3.12	+2.26
Mg^{II}	+1.231			4.07	+2.07	3.57	+2.04	2.91	+2.05
Mn^{II}	+0.824	3.36	+ .79	2.79	+0.79	2.32	+0.79	1.65	+0.79
Al^{III}	+1.015	4.03	+1.46	3.45	+1.45	3.00	+1.47	2.31	+1.45
Zn^{II}	+0.503	3.04	+0.47	2.46	+0.46	1.99	+0.46	1.32	+0.46
Cd^{II}	+0.174	2.69	+0.12	2.09	+0.09	1.65	+0.12	1.08	+0.22
Fe^{II}	+0.087	2.77	+0.20	2.18	+0.18	1.71	+0.18	1.04	+0.18
Fe^{III}		2.43	—0.14	1.85	—0.15	1.38	—0.15	.72	—0.14
Ni^{II}	—0.020	2.63	+0.06	2.04	+0.04	1.57	+0.04	.90	+0.04
Co^{II}	—0.015	2.66	+0.09	2.07	+0.07	1.60	+0.07	.89	+0.03
H^{I}	—0.249	2.18	—0.39	1.71	—0.29	1.24	—0.29	.57	—0.29
Cu^{II}	—0.550	1.95	—0.61	1.36	—0.64	.89	—0.64		
Hg^{II}				1.10	—0.90	.81	—0.62		
Pt^{IV}	—1.140			.87	—1.13	.57	—0.96		
Au^{III}	—1.356			.39	—1.61	.24	—1.29		

These values, given in Table I, are plotted on Plate I, with the voltages of decomposition as abscissæ and the single potentials of the metals as ordinates. This diagram represents the well-known additive law. In it, there will be noticed, that equal increments mark the displacement of one metal by another metal or one halogen element by another halogen element. This results in two sets of parallel lines. This diagram can be used in the calculation of any one of the three factors—the total decomposition voltage, single

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potential of the anion, or single potential of the cation, when the other two factors are known. Some very useful results can be obtained in this way. It must, however, be remembered that the formation of *normal* salts in *dilute aqueous* solution is postulated.

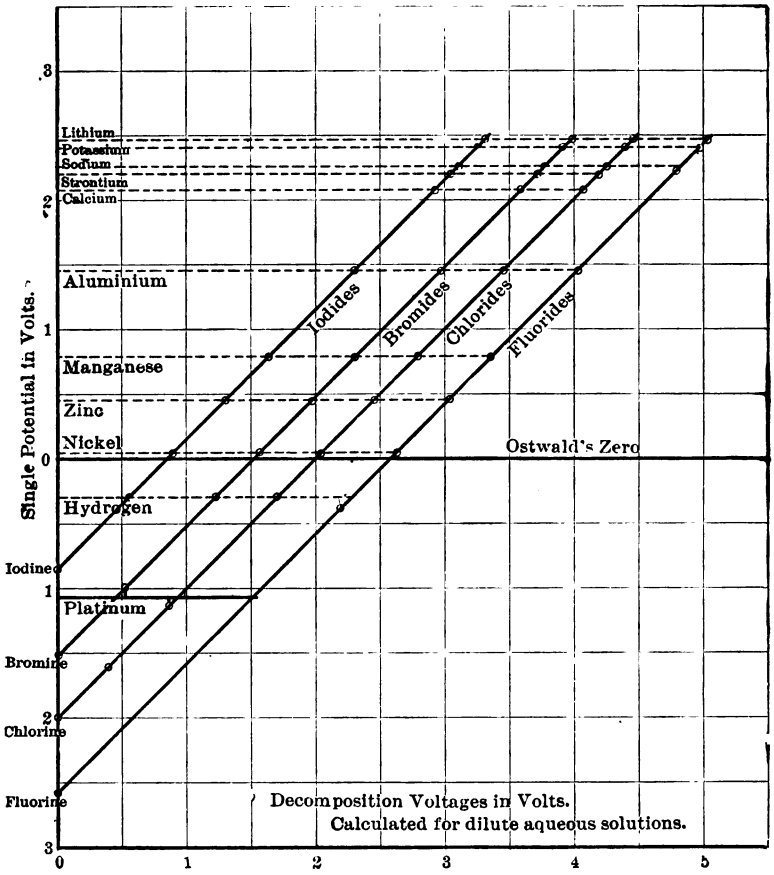

PLATE I.

A careful comparison of these values among themselves and with the experimental single potentials shows the value and the reliability of the method. Generally, the variations do not exceed one-tenth of a volt. This is remarkable when the many sources of error in obtaining thermal data and electrode potentials are con-

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sidered. Differences in the physical condition (such as mechanical strains, crystalline structure, etc.) of both the salt and of its original elements offer important sources of error. The experimental single potentials of cathions have been shown to compare favorably with calculated values. The anion single potentials will now be considered.

The experimental data was taken in the same manner and with the same apparatus as that described in several previous papers.[1]

The first halogen element, fluorine, has been given the low single potential of —1.98 volt by R. Abegg and Cl. Immerwahr[2] from decomposition voltage. This is 0.59 volt below the theoretical. In Table III, I give an experimental discharge (—2.00 volts) of the anode at a current density of about 0.030 amp. per square centimeter. This value[3] agrees with the above experimental result.

But a little consideration will show that the chemical reaction taking place is not that of the liberation of fluorine, but of oxygen and ozone. As the current density increases the products change from oxygen free from ozone[4] to oxygen containing a great deal of ozone and then to the primary product, the fluorine. These different chemical reactions appear perfectly natural when we consider that Moissan noticed a yield of 20 per cent. ozone from the reaction of gaseous fluorine upon water. From these considerations, it is obvious that to get the single potential of fluorine a much higher current density is necessary.

This I secured by taking a fine platinum wire fused in glass and broken off short. With 10 volts, .020 amp. was passed through a normal solution of potassium fluorine with this electrode as anode. This gave a current density of about 2 amp. per square centimeter. The discharge potential of the anode was —2.53 volts. This experiment was repeated with another slightly larger electrode and with a new solution. The anode discharge potential was nearly as high as the above value. The theoretical single

[1] Patten and Mott, Trans. Amer. Electrochem. Soc., Vol. III, p. 317.
Patten and Mott, "Decomposition Curves of Lithium Chloride in Alcohols and the Electro-deposition of Lithium." Jour. of Phys. Chem., Vol. VIII, p. 153, March, 1904.

[2] Zeit. Phy. Chem., 1900, 32, 142.

[3] The polarizations, obtained by the method of discharge potential, give low values because of the time and current required for the readings. The allowable time depends entirely on the amount and stability of the products which cause the polarization. For example, compare the discharge potentials of zinc and fluorine. The latter is given off only in small quantities and is rapidly used up by the solution. Discharge potentials given in this paper required an interval of about one-tenth of a second for their experimental determination.

[4] Gore, The Art of Electrolytic Separation, etc., p. 98.

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potential of fluorine (—2.57 volts) compares favorably with this experimental value.

Another check on this value follows from a number of curves of total polarization. One of these is given in Table II, and plotted on Plate II.

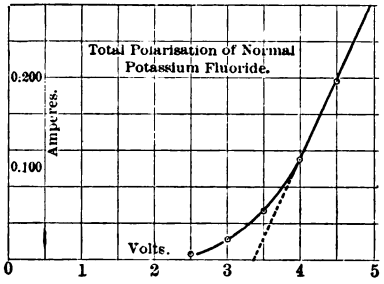

PLATE II.

TABLE II.

DECOMPOSITION—POINT CURVE FOR NORMAL POTASSIUM FLUORIDE.

Total Volts	Ampères
5.00	.300
4.50	.198
4.00	.112
3.50	.054
3.00	.022
2.50	.005

The CR line produced shows a total polarization of 3.3 volts. The cathode polarization would not exceed +.65 volt (see Table III); so the anode polarization amounts to —2.65 volts.

Other halogen salts (Table III) of potassium were electrolyzed. The anode curves are plotted on Plate III.

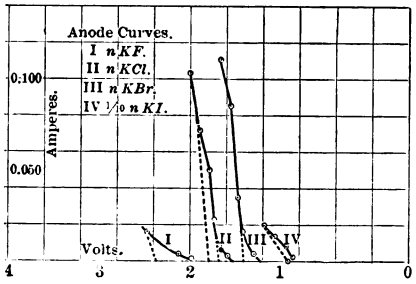

PLATE III.

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The anode curve of potassium fluoride shows a polarization equal to —2.4 volts (current density about 0.020 amp. per square centimeter). The CR line was obtained from the cathode curve and the total curve. The curve itself is not satisfactory because of its incompleteness, and is only reproduced for the sake of comparison.

TABLE III.

Total Volts.	Ampères.	Anode.	Cathode.
		n K F.	
2.00	.002	—1.97	
2.50	.004	—2.13	+.40
3.20	.016	—2.45	+.65
3.80	.100		+.93
Discharge	.100	—2.00	
		n K Cl.	
2.00	.002	—1.59	+.39
2.20	.005	—1.66	+.54
2.40	.023	—1.73	+.66
2.60	.050	—1.79	+.77
2.80	.072	—1.90	+.86
3.00	.103	—2.00	+.95
Discharge	.103	—1.76	
		n K Br.	
1.80	.004	—1.29	+.47
2.04	.017	—1.42	+.60
2.20	.035	—1.48	+.66
2.40	.085	—1.56	+.79
2.60	.110	—1.67	+.89
2.80	.172	—1.70	+.96
Discharge	.172	—1.34	
		1-10 n K I.	
1.40	.003	— .87	+.50
1.60	.008	— .94	+.63
1.80	.014	—1.06	+.71
2.00	.020	—1.17	+.85
Discharge	.020	— .90	

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The potential of chlorine has created much discussion[1] in electrochemical circles. A solution of chlorine can hardly be considered of the same nature as those of hydrogen or nitrogen in water, since the reaction of chlorine on water to form hypochlorous acid and hydrochloric acid would yield about the same heat as that found in dissolving chlorine in water. The equilibrium that might exist in the presence of water, chlorine, hydrochloric acid and hypochlorous acid has been well discussed by Müller and others.[2] So at the anode, we may expect the potential to be mainly due to these oxy-compounds of chlorine, which, of course, as they increase the conductivity[3] of the solution, therefore, tend to furnish primary products containing oxygen. So it is not surprising that the observed anode potentials are not those of chlorine, but of oxy-chlorine compounds and of oxygen.

Using the electrode, consisting of a platinum point fused in glass (the same as used in the fluorine experiment), I obtained a discharge potential of —1.81 volts. A current of 0.050 amp. (a current density of about 4 amp. per square centimeter) was passed by 11½ volts, through a twice normal solution of potassium chloride.

This calculated value of —2.00 volts applies only to dilute solution from which experiments show oxygen separates on electrolysis, and not chlorine; therefore, chlorine must have a single potential *greater* than that of oxygen in acid solution.

The anode curve (Plate III) for normal potassium bromide gives a polarization of about —1.40 volts. Bromine separates out on the electrode as can be seen from its brown color. At higher current densities, obtained with the platinum point fused in glass, the anode discharge potential was found to be —1.43 volts with a current of 0.050 amp. and a voltage of 11½ volts. This value is 0.10 of a volt below the theoretical (—1.53 volt).

Potassium iodide, with this same apparatus, gave an anode discharge potential of —.91 volts. The iodine was seen to deposit, and

[1] Gockel,—Zeitschr. Phys. Chem., 1900. **32**: 607.
Akunoff,—Zeit. Elektrochem., 1900, **7**: 354.
Lorenz and Wehrlin,—Zeit. Elektrochem., 1900, **6**: 339, 408, 419, 437, 445.
Müller,—Zeit. Elektrochem., 1900, **6**: 573. 581. 1901, **7**: 750. 1902, **8**: 425.
Foerster and Müller,—Zeit. Elektrochem., 1903, **9**: 171, 195.

[2] See Richardson, Jour. Chem. Soc., 1903, **83**: 380.

[3] In some preliminary work on specific conductivity two years ago, I noticed that chlorine water (saturated) has a very considerable conductivity, 17.0 x 10^{-3} reciprocal ohms per cubic centimeter at 25.0° C.

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this caused a rapid decrease in current flow. The pressure used was 11½ volts. This discharge potential is 0.04 volts higher than the theoretical value (—.87 volts). Bancroft[1] gives the polarization of iodine, dissolved in potassium iodide, as —0.888 volt. This is still closer to the theoretical value.

Hence the calculated single potentials of the halogen elements checks reasonably well with the experimental data, and the additive law applies to halogen salts in dilute aqueous solution. So we are able to predict the single potentials of metals,[2] the single potentials of non-metals and the heat of formation of their salts. A special application of this last case will now be considered.

LAW OF SOLUBILITY AND HEAT OF SOLUTION.—The calculated decomposition voltages for *nearly insoluble*[3] salts, for example, AgCl, CaF_2, $BaSO_4$, are much *smaller* than for the decomposition voltages as calculated from thermal data for the solid salt. This means that there is a large negative heat of solution; that is, the salt dissolves with a large absorption of heat. These calculations refer to ordinary temperatures.

In Table IV, there is a list of the voltages due to the heat of solution. Hydriodic acid has the largest heat of solution, and the voltage added to its decomposition voltage because of this heat of solution is 1.04 volt. The following points will be noted from this table: The iodides of the alkali metals dissolve with evolution of the greatest heat. They are also the most soluble of the halogen salts. The greater the atomic weight of the metal the smaller or more negative the heat of solution and the more insoluble the salt. With halogen salts of the alkali metals and alkaline earth metals, the solubility increases with the increase of the atomic weight of the halogen element. The heat of solution also follows this order.

With the uni-valent salts of Cu, Ag, Au, the solubility and heat of solution of the salt decreases both with a decrease in the atomic weight of the metal element and a decrease in the atomic weight of the halogen element. For example, silver fluoride has a positive heat of solution and is classed as a soluble salt. Silver iodide is the most insoluble of all the halogen salts of silver and has the most negative, calculated heat of solution.

[1] Zeit. Phy. Chem., 1894, XIV: 193.

[2] Considerations set forth in this paper show that Wilsmore's (Zeit. Phy. Chem., 1900, **35**, 391) calculated values for alkali and alkaline earth metals are most incorrect.

[3] Compare Nernst, Ber. d. d. chem. Ges. 1897, **30**, 1557.

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TABLE IV.

HEATS OF SOLUTION IN TERMS OF VOLTS.

			Fluorides.	Chlorides.	Bromides.	Iodides.	
Group I.	Sub-group A.	H^{I}	+0.20	+0.756	+0.94	+1.040	
		Li^{I}	.....	+0.365	+0.47	+0.66	
		Na^{II}	—0.023	—0.046	—0.01	—0.049	
		K^{I}	—0.147	—0.196	—0.23	—0.23	
		Rb^{I}	.....	.....	.....	.....	
		Cs^{I}	.....	.....	.....	.....	
	Sub group B.	Cu^{I}	.....	—0.15*	.....	—0.49*	
		Ag^{I}	+0.114	—0.31*	—0.55*	—0.81*	
		Au^{I}	.....	.....	.....	.....	
Group II.	Sub-group A.	Be^{II}	.....	.....	.....	.....	
		Mg^{II}	+0.04*	+0.564	+0.94	+1.085	
		Ca^{II}	—0.07*	+0.38	0.53	+0.603	
		Sr^{II}	—0.10*	+0.24	0.35	+0.45	
		Ba^{II}	—0.025	+0.04	0.11	+0.23	
	Sub-group B.	Zn^{II}	.....	+0.34	+0.33	+0.25	
		Cd^{II}	.....	+0.08	—0.01	—0.02	
		Hg^{II}	.....	—0.06	—0.07	—0.60*	(—0.69)°*

* = calculated.

° This second value is calculated for the red mercuric iodide. Two solid phases are characteristic of the halogen salts of this sub-group.

The alkaline earth metals show relationships exactly parallel to those shown for the alkali metals. The periodic law applied to Groups I and II is borne out with surprising regularity.

It would be interesting to learn how this heat of solution is distributed between the anion potential and the cathion potential.

IN CONCLUSION.—Experimental data for the single potentials of fluorine, chlorine, bromine and iodine have been obtained, showing the value of the additive law for both anions and cathions. The additive law holds much better for dilute aqueous solutions than for solid salts. Solid salts may, in different forms, possess very different amounts of energy; for example, amorphous silver iodide has a heat of formation of 8.6 large calories, while the crystalline variety has a heat of formation of 14.2 large calories.

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This introduces a difference of 0.33 volts in their respective decomposition voltages.

The difference between the decomposition voltage of the solid salt and of the dissolved salt represents the heat of solution or the energy of the reaction resulting from the affinity of the salt for the solvent. Other solvents than water give very different heats of solution. Quantitative work in this field is scarce and is much to be desired.

It is shown in this paper that heats of solution of insoluble[1] salts can be calculated, and the results add force to the law that:

Solubility[2] is largely determined by the mutual affinity[3] of the solvent and solute as represented by the heat of solution.

It is my pleasure to give my hearty thanks to Dr. Patten and Professor Burgess for many favors extended me in carrying out this work.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

DR. R. GAHL: The friends of the dissociation theory will certainly appreciate that the author of this paper has taken pains to investigate one of the principles which follow from the dissociation theory, that is, the additive law for decomposition voltages. It is very interesting that the author could prove this law by his experiments.

But I think, that generally exception will be taken to the other result which the author reached, "that the difference in the decomposition voltage of a solid salt and of a dissolved salt represents the heat of solution or the energy of the action resulting from the affinity of the salt for the solvent." This result does not agree

[1] No salt can be said to be absolutely insoluble; if it were, the supposition of a heat of solution would be absurd.

[2] Most salts that contain water of crystalization are known to have a positive heat of solution for the anhydrous salt.

[3] The relationship between heat of solution and solubility as set forth by the author of this paper is totally different from some ideas on the relation of electroaffinity and solubility, given by Abegg and Bodländer, which have met severe criticism from Locke and others.

See Abegg and Bodländer, Zeitschr. anorg. Chem., 1899, **20**, 453.
Locke, Am. Chem. J., 1902 **27**, 105.
Abegg and Bodländer, Am. Chem. J., **28**, 220.

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with thermodynamics, which shows that a salt in equilibrium with its saturated solution requires the same amount of free energy for decomposition in the solid state and in solution. Therefore, if we speak at all about the decomposition voltage of a solid salt, we have to take it as high as of the saturated solution. Really we cannot decompose the solid salt, but only can calculate a theoretical decomposition voltage, knowing that it is an expression for the difference in free energy.

This wrong result of the author was reached by using the formula of Thomson for the whole Helmholtz formula. There is no doubt that it is useful sometimes for practical purposes to calculate with the heat of reaction, if the whole free energy is not known, but one has always to bear in mind that this way is not quite correct and that it may lead to results which do not agree with thermodynamics. For this reason, it seems to me that the voltages derived from the heat of reaction should not be, as is still frequently done, called theoretical. My opinion is, that a calculated voltage should only be named theoretically, if it is derived from a valid theory and not from a theory which we know to give sometimes very wrong results.

Regarding this paper I cannot help feeling that an application of the Nernst formula would have been more useful than the application of Thomson's rule. At least I should like to state that the use of solution tensions which causes blindness against thermodynamical facts in the author's opinion is not the only cause for such blindness.

Mr. W. R. Mott: I cannot reply in full, at present, to the gentleman's remarks. But the energy of the reaction between the solvent and solute must be considered in electrolysis just as much as the energy due to the formation of the salt in the solid state. That there is a real affinity of a chemical nature between solvent and solute has been proved by Kahlenberg and his able assistants. References cited on page 73, show that Nernst's idea of solution tension is not tenable and that more attention should be paid to the real chemical reactions.

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DISCUSSION COMMUNICATED AFTER ADJOURNMENT, BY W. R. MOTT.

MR. W. R. MOTT: Dr. Gahl has said that the heat of solution is essentially an entropy factor; but he has not proved it or even referred to any one proving it. That the second law of thermodynamics is true, all must admit; but adequate proof that the temperature coefficients of the cell and of the half cell depend largely upon heat of solution has not been given by Dr. Gahl. Experiments upon non-aqueous solutions where the heat of solution varies greatly with the solvent, are needed for a thorough discussion of this point. Such experiments as have been made in this direction show that the so-called solution tension of a metal varies greatly with the solvent and that it depends upon the heat of solution.

Kahlenberg[1] has found that cadmium has a high single potential against $\frac{n}{10}$ CdI_2 in normal propyl amine (+0.479) and in isobutyl amine (+0.353); but, in water (+0.182) and other solvents a much lower value. Where are we to look for the source of this great difference? It is unsatisfactory to try to explain it by a solution tension that depends upon the solvent as well as upon the metal and by an osmotic pressure that depends upon both dissociation and association. The real solution to the problem is gained from the following quotations. "In normal propyl amine, cadmium iodide dissolves with violent action and evolution of much heat; in isobutyl amine the reaction is less violent." "The difference of potential between a metal and a solution is undoubtedly determined by the chemical affinity existing between the metal and the solution."

That the dilution law may not be involved in these considerations, I would again refer to the fact that data given by me was for concentrations between normal and tenth normal. This is the universal practice. For the further refutation of Dr. Gahl's remarks I give for comparison the following table of the results

[1] Trans. Am. Electrochem. Soc., Vol. II, p. 89 1902. See also J. Phys. Chem., 3, 379 (1899); 4. 709 (1900).

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obtained by various scientists. This series is quoted from Billitzer.[1] Under the column headed Billitzer, are given Wilsmore's results referred to Billitzer's zero. This zero is about 0.75 volt above Ostwald's zero to which the other potentials are referred. My results, here tabulated for the sake of comparison, are calculated in my paper and are there *experimentally* confirmed.

In regard to this new zero, will Krüger find new material for criticizing Lehfeldt?

TABLE I.

"ABSOLUTE" ELECTROLYTIC POTENTIAL.

Element	Ostwald	Billitzer	Mott
K	(+2.92)	(+3.66)	+2.38
Ba	(+2.54)	(+3.28)	——
Mg	+1.214?	+1.95?	+2.07
Mn	+0.798	+1.54	+0.79
Zn	+0.493	+1.23	+0.46
Cd	+0.143	+0.88	+0.09
Fe	+0.063	+0.80	+0.18
Tl	+0.045	+0.79	——
Co	—0.045	+0.69	+0.07
Ni	—0.049	+0.69	+0.04
Sn	<—0.085	——	——
Pb	—0.129	+0.61	——
H	—0.277	+0.46	—0.29
Cu	—0.606	+0.13	—0.64
As	<—0.570	——	——
Hg	—1.027	—0.29	—0.90
Ag	—1.048	—0.31	——
Pd	<—1.066	<—0.33	——
Pt	<—1.140	<—0.40	—1.13
Au	<—1.356	<—0.62	—1.61
Fl	(—2.24)	(—1.5)	—2.53
Cl	—1.694	—0.95	—2.00
Br	—1.270	—0.53	—1.53
I	—0.797	—0.06	—0.87

[1] Dr. Jean Billitzer: Sitzungberichte der kaiserlichen Akademie der Wissenschaften. Mathematish-Naturwissenschaftliche Klasse. Abteilung IIa. Vol. 112 pages 95-138, March 12, 1903.

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In conclusion, it has been the general practice (Wilsmore, Naumann, etc.,) to include the heat of solution in voltage calculation from thermal data. Further, Jahn's results do not show that the entropy factor is so very large or that heat of solution is its chief source. So we may conclude that *experimental* investigation of the *real chemical reactions,* and of the *real temperature coefficients* is the hope of future progress along these lines.

Dr. Gahl says that the free energy is always the same for a salt and for a solution saturated with that salt. This is incorrect. What Gibbs proved was that in order that two phases may exist in equilibrium with each other, for example, a solid salt and a solution of the same, they must be at the same chemical potential. The energy distribution is entirely another matter. This mistake would not have been made, had experiments been tried upon the decomposition voltages (anode and cathode potentials) with a saturated solution of the same salt in different solvents. To say that the solvent does not affect the free energy is a dangerous mistake.

Dr. Gahl thinks that an application of the Nernst formula would have been much more useful. Perhaps this may be true when the Nernst formula has been modified to express completely the thermodynamics of the case (energy due to volume changes are assumed constant), and further when it is clothed in the experimental facts in such a way that the free and bound energy due to the affinity of solvent and solute is used in place of a gas-like pressure, due to a mixture of molecules and ions in a liquid whose nature does not appear in the formula. However, for concentration changes, Nernst's formula is useful, being a partial expression of empirical facts upon whose theoretical interpretation the scientific world is divided.

Wilsmore's results have been obtained particularly from the viewpoint given by the ionisation theory. They are quoted by Nernst and Ostwald. Wilsmore takes particular pains to include the heat of solution in the heat of formation that he uses to calculate the total decomposition voltage. He applies the additive law and subtracts the single potential of the chlorine from the total decomposition voltage of the chloride in order to calculate the single potential of the metal. This is not, in principle, different from the method used by me. But our respective values of the

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single potential of chlorine are very different. It is unfortunate that Wilsmore did not quote two separate series of values, the calculated values and the observed values. His calculated values are given practically, only for metals which at that time had not been experimentally investigated.

TABLE II.

WILSMORE'S "ABSOLUTE" ELECTROLYTIC POTENTIALS.[1]

(Potentials in parentheses are calculated.)

Metals	Potentials
K	(+2.92)
Na	(+2.54)
Ba	(+2.54)
Sr	(+2.49)
Ca	(+2.28)
Mg	(+2.26)
Mg	+1.214?
Al	+0.999?
Mn	+0.798
Zn	+0.493
Cd	+0.143
Fe	+0.063
Tl	+0.045
Co	—0.045
Ni	—0.049
Sn	<—0.085
Pb	—0.129
H	—0.277
Cu	—0.606
As	<—0.570
Bi	<—0.668
Sb	<—0.743
Hg	—1.027
Ag	—1.048
Pd	<—1.066
Pt	<—1.140
Au	<—1.356

[1] Referred to Ostwald's zero.

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Non-Metals	Potentials
Fl	(—2.24)
Cl	—1.694
Br	—1.270
I	—0.797
O	—1.396?

Experimental values for sodium, potassium, lithium and similar metals are at hand and they do not fulfill, even roughly (within a tenth of a volt), the predictions of Wilsmore. But this is no more significant than that other metals whose single potentials are known, do not check, even roughly, values calculated by Wilsmore's method. The calculated values average 0.3 volt too high, showing conclusively that a chlorine value of (—2.00) volts is the value that should be used in place of Wilsmore's chlorine value (—1.694).

In conclusion, I wish to emphasize the experimental side of my paper, so I give the following table:

	Single Potentials in Volts	
Halogen Element	Calculated	Experimental
Fluorine	—2.57	—2.53
Chlorine	—2.00	<—1.81
Bromine	—1.53	—1.43
Iodine	—0.87	—0.91

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 8, 1904, Vice-President Carhart in the Chair.

THE COMPOSITION AND RESOLUTION OF VOLTAGES.

By Joseph W. Richards.

When chemical action is the source of an electromotive force, the cell in which this takes place furnishes us an electromotive force on open circuit equal to a certain maximum value, which we may call the electromotive force of the cell. If we reverse the direction of the current by a superior externally-applied potential, an amount of potential will disappear in the cell equal to the electromotive force of the same on open circuit, and corresponding, with more or less approximation, to the chemical work done in the cell.

These principles are of simple application when only one substance is being dissolved at the anode and one substance deposited out at the cathode. In such cases, the quantity of material dissolved or deposited being assumed equal to what is required by Faraday's law, at 100 per cent. efficiency of solution and of deposition, it is easy to calculate the electromotive force which should be generated or absorbed to correspond with the chemical energy liberated or absorbed. (We will consider these quantities independently of whatever potential may be gained or lost by thermoelectric influences.)

However, such simple actions are not always the only ones occurring. When impure metal is used as anode in electrolytic refining, several metals may, and often do, go simultaneously into solution, while practically only the one metal is being deposited, corresponding to the generation of differing electromotive forces, if each metal went into solution by itself. When the impurities accumulate to a certain degree, depending upon the current density used, a proportion of these is simultaneously deposited with the principal metal, and in this case the current is again doing varying quantities of chemical work, corresponding, if each were

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deposited separately, to different potentials disappearing in the different amounts of chemical work done.

We thus have, in electrolysis, besides the drop of potential due to overcoming ohmic resistance (equal to R x C) and besides the potential lost or gained by Peltier effect ($T\frac{de}{dt}$), the varying voltage E^d, gained or lost by chemical action, and in *practical electrolysis* this factor is, in almost every instance, a composite one, as has been explained above, and its correct calculation involves what I have termed the composition or the resolution of different voltages.

Composition of voltages at the Anode.—If, for convenience of discussion, we assume that we are dealing with dilute solutions as electrolytes, and use the values of the single potentials of the metals, as derived from their thermochemical constants, it will simplify the calculations.

Assume that we are refining an impure copper containing 90 per cent of copper, 5 per cent. of iron, 1 per cent. of nickel and 1 per cent. of zinc, and that these all go into solution, but that only copper is precipitated, and that at an ampère efficiency of 100 per cent. For every 96,540 coulombs passing there will be deposited 31.80 grammes of copper, but there will be dissolved the following quantities:

29.275	grammes	of copper,	requiring	92.06	per cent.	of the	current.
1.625	"	" iron,	"	5.82	"	"	"
0.325	"	" nickel,	"	1.11	"	"	"
0.325	"	" zinc,	"	1.01	"	"	"
31.550	"	altogether,	"	100.00	"	"	"

If we take as the single potentials of the metals going into solution—(Richards, these Transactions, Vol. IV, p. 142):

copper	— 0.382	volts.
iron	+ 0.434	"
nickel	+ 0.295	"
zinc	+ 0.707	"

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the excess of voltage furnished by those fractions of the current which dissolve iron, nickel and zinc, above that needed for depositing copper, are respectively:

dissolving iron	+ 0.816	volts.
" nickel	+ 0.677	"
" zinc	+ 1.089	"

and the excess voltage delivered as electromotive force to the circuit will be the above surpluses multiplied by the respective fractions of the current thus employed, viz:

$$\left.\begin{array}{l} 0.816 \times 0.0582 = 0.0475 \\ 0.677 \times 0.0111 = 0.0075 \\ 1.089 \times 0.0101 = 0.0110 \end{array}\right\} + 0.0655 \text{ volts.}$$

The solution of the anode is thus seen, by the principle of composition of voltages, to add an electromotive force of some 0.065 volts to the circuit. With 100 baths in circuit, this assists the dynamo to the extent of 6.5 volts, which is a respectable percentage upon the total power used.

To give one more illustration of this principle, and to make the calculation in another manner, although exactly on the same principle, let us consider the Browne process of using a copper-nickel anode in a solution of cuprous chloride, dissolving both copper and nickel and depositing only copper. The anode contains nearly equal parts of nickel and copper, and is represented with sufficient closeness by the formula Cu Ni. The whole reaction on passing the current is shown by the equation

$$3CuCl + CuNi = 3Cu + CuCl + NiCl^2$$

In short, on passing three Faradays (3 times 96,540 conlombs) of electricity through this solution, all the current deposits copper, one-third of the current dissolves copper and two-thirds dissolves nickel. We have to omit from our calculations the unknown heat of formation of the alloy CuNi, and then we have the chemical energy involved in the above equation as being

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Absorbed

$$(Cu, Cl, aq) = 3 \times 31{,}100 = 93{,}300 \text{ calories.}$$

Evolved

1(Cu, Cl, aq) =	31,100		
1(Ni, Cl^2, aq) =	93,900		
		=125,000	"
Excess		31,700	"
" per 1 chemical equivalent		10,570	"
Electromotive force corresponding		0.459	volts.

This is only another way of figuring out the principle that if the difference between the heats of formation of 1 equivalent of nickel chloride and cuprous chloride is 15,850 calories, that if all the current dissolved nickel, the potential contributed to the circuit would be 0.688 volts, but since only two-thirds of the current dissolves nickel, the electromotive force contributed is ⅓ times 0 + ⅔ times 0.688, or 0.459 volts.

Resolution of voltages at the Cathode.—When a compound electrolyte is decomposed, the weaker metals alone are deposited if they are present in excess and a moderate current density is used. If solutions are used in which the stronger metals are in excess, both weak and strong metals are simultaneously deposited, when the current density exceeds a limiting value, depending on the relative proportions of the weak and strong metals, the temperature and activity of circulation. This is as true of hydrogen as it is of the metals, *when the solution contains free acid,* and our discussion therefore covers the important case of the simultaneous liberation of hydrogen and the deposition of a metal.

Tomassi makes the statement that when over 30 molecules of copper nitrate is present to 1 molecule of silver nitrate, in an electrolyte, that copper begins to be deposited with the silver, and that when the solution contains 87 molecules of copper nitrate to 2 molecules of silver nitrate, the deposit is one atom of copper to one atom of silver. Two cases may be worth considering: (1) when the anode is copper, immersed in a copper nitrate solution, and (2) when the anode is silver, immersed in a copper nitrate or silver

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nitrate solution, or a mixture of the two nitrates. In case (1) the reaction will be

$$87Cu\,(NO^3)^2 + 2Ag\,NO^3 + 3Cu = 2CuAg + 88Cu(NO^3)^2$$

all in aqueous solution, or, expressed more briefly:

$$2AgNO^3 + 3Cu = 2CuAg + Cu\,(NO^3)^2.$$

Neglecting the heat of formation of the alloy 2CuAg, which is unknown, the net heat balance of above equation is:

Absorbed		
$2(Ag, N, O_3, aq)$	$= 2 \times 23{,}000 = 46{,}000$	calories.
Evolved		
$(Cu, N^2, O^6, aq =$	$= 81{,}300$	"
Excess evolved	35,300	"
" per "Faraday" passing	5,880	"
Electromotive force corresponding	0.255 volts.	

This arrangement should, therefore, act as a battery with an electromotive force of 0.225 volts on open circuit, whereas a cell composed of Ag, $AgNO^3$, $Cu(NO^3)^2$, Cu should give 0.765 volts from the chemical energy involved.

In case (2), with silver anode, the reaction would be practically

$$87Cu(NO^3)^2 + 2AgNO^3 + 6Ag = 2CuAg + 6AgNO^3 + 85Cu(NO^3)^2.$$

or, expressed briefly

$$2Cu(NO^3)^2 + 6Ag = 2CuAg + 4AgNO^3.$$

Proceeding as before, the net heat involved is

Absorbed		
$2(Cu, N^2, O^6, aq)$	$= 2 \times 81{,}300 = 162{,}600$	calories.
Evolved		
$4(Ag, N, O^3, aq)$	$= 4 \times 23{,}000 = 92{,}000$	"
Excess absorbed	70,600	"
" per "Faraday" passing	11,770	"
Potential absorbed, corresponding	0.51 volts	

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It will be observed that the substitution of silver for copper as the anode makes the difference between + 0.255 volts and — 0.51 volts, or a total difference of 0.765 volts, which corresponds to that of the $Ag\text{-}AgNO^3—Cu(NO^3)^2—Cu$ cell.

We may express case (1) in the manner of saying that one-third of the current deposits silver, an operation evolving 0.765 volts, and two-thirds deposits copper, an operation evolving 0 volts, and therefore the net voltage evolved is $0.765 \times \frac{1}{3} = 0.255$ volts. We may similarly express case (2) by saying that one-third of the current deposits silver, an operation evolving or absorbing 0 volts, and two-thirds deposits copper, an operation absorbing 0.765 volts, and therefore the net voltage absorbed is $0.765 \times \frac{2}{3} = 0.510$ volts.

The proper basis to rest such calculations upon is undoubtedly the energy equivalents, viz., to say that in case (1) one-third of the current evolves 0.765 joules of energy for each coulomb thus depositing silver, while two-thirds of the current evolves 0 joules, making a net average of 0.255 joules evolved for each coulomb passing, and thus necessarily furnishing current at a potential of 0.255 volts. In case (2) one-third of the current absorbs 0 joules, and two-thirds absorbs 0.765 joules for each coulomb thus depositing copper, making a net average of 0.51 joules absorbed for each coulomb passing, and thus necessarily absorbing a potential of 0.51 volts.

Passing finally to the important case of the simultaneous liberation of hydrogen and deposition of metal, assume that in depositing copper from acidulated copper sulphate, 20 per cent. of the current is liberating hydrogen and 80 per cent. depositing copper, what is the extra voltage absorbed as chemical work over the case when only copper is deposited, assuming all other chemical actions (such as solution at the anode) unchanged?

The reaction will be

$$4CuSO^4 + H^2SO^4 + 5Cu = 4Cu + H^2 + 5CuSO^4$$

or, more briefly

$$H^2SO^4 + 5Cu = 4Cu + H^2 + CuSO^4$$

and the net heat balance, assuming all in dilute solution, is

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Absorbed		
(H^2, S, O^4, aq)	= 210,100	calories.
Evolved		
(Cu, S, O^4, aq)	= 197,000	"
Excess absorbed	= 12,600	"
" " per "Faraday"	= 1,260	"
Potential absorbed, corresponding	= 0.055	volts.

If all the current were developing hydrogen, while no copper was being deposited, the increase of voltage absorbed would be $0.055 \times 5 = 0.275$ volts, corresponding to the whole difference of chemical energy between hydrogen and copper. Such a condition could only exist, however, when all the copper had disappeared from the cathodic solution, and the current was all evolving hydrogen,—as occurs towards the end of an analytical determination of copper.

If I have made clear the phenomena which we have been considering, and the principle of composition and resolution of voltages which so frequently applies to cases of practical electrolysis, I will venture to make the further statement that the principle is really that of the composition and resolution of the different amounts of energy involved in the different chemical reactions taking place or being produced, and that the expression of these as voltages is a secondary or derived mode of expression which really has its counterpart in natural phenomena only when the current is performing one simple, plain chemical reaction. Whenever, as is frequently the case, two or more elements are simultaneously dissolved or deposited, the voltages characteristic of the solution or deposition of each element lose all physical significance, and the energy principle, the amount of work done, remains as our only safe guide and basis of calculation.

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DISCUSSION.

MR. L. ADDICKS: I think this paper brings out in one way what happens when rough copper results from an endeavor to increase the current density in the ordinary copper refining cell. The rough copper is largely produced by hydrogen at the cathode, and we endeavor to meet this by increasing the circulation with the object of increasing the proportion of copper ions present to those of hydrogen; and of course the more rapidly we plate the copper out, the more rapid must be the supply of copper ions to maintain the balance.

MR. W. R. MOTT: There are various points that might introduce variations into these calculations. One of these is as regards the concentration polarization. If you take a pure copper anode and a pure copper cathode and electrolyze, we expect certain concentration polarizations. Secondly, at the anode, we have a solvent action independent of the current, in some cases due to the action of sulphuric acid present; and so the total amount of coulombs that have passed are not always represented by the metal that is dissolved. Thirdly, we have the heat due to the alloying effect, which is quite large in the case of brass,[1] amounting to about 0.7 volt. Fourthly, in regard to the hydrogen, if you take certain cathode metals, the hydrogen comes out at only high voltages, due to the over-voltage or Caspari effect. So it is a question as to how experimental results on the simultaneous separation of copper and hydrogen can be used to check these calculated values.

MR. CARL HERING: I understand that Professor Richards' ideas are based on thoretical considerations only, as distinguished from practical measurements. I understand also that the calculations are simply based on the principle of the conservation of energy. That is, he calculates how much energy is required or is given up, and from that he deduces the average voltage, or more correctly, the average of several different voltages. From the theoretical standpoint the idea is very attractive; and it would be interesting if it could be proved that it were correct; but I am inclined to believe that practice has not yet shown that it is quite correct. It is a little hard to believe that you can ever get zinc

[1] See Herschowitsch: Zeit. phys. Chem., **27**, 123-126 (1898).
The Electrician, **43**, 883-884.
Jahrbuch der Electrochemie, **6**, 36 (1899).
Patten and Mott: Trans. Am. Electrochem. Soc., **3**, 317, (1903).

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deposited together with other metals, with a voltage less than that required to deposit zinc alone; although, according to Professor Richards' calculations, this would be possible. At the same time, I believe there are practical data which seem at least to indicate that this is the case.

It seems to me, therefore, that this is something which has not yet been proved to be correct. There are other factors which enter, which, I think, will produce quite different results, and will vitiate the calculation very greatly. Take, for instance, the very illustration he has on the board, in which there is both zinc and iron on the anode. He makes a theoretical calculation, as though that were all going to go on as he believed it will; but as a matter of fact, I think it will be found that in such a case the zinc would dissolve by local action on the anode and the energy that dissolved the zinc would therefore not appear in his calculation at all; because the dissolution of the zinc would go on whether there was current flowing or not; because we know perfectly well that when zinc and iron are in contact, and put into an acid solution, there will be local action which will dissolve the zinc and cause hydrogen to be deposited on the iron, or reduce any iron oxide that may exist. It therefore hardly seems that in such a calculation we could include such metals as zinc, which would be dissolved by local action alone. Then there is the resistance factor, that is, the voltage due to the resistance of the solution; also the voltage which one of the previous speakers spoke of, called the overvoltage. These two factors may be so great as to completely obscure this small voltage which Professor Richards has calculated. It is therefore a question whether his method would have any great value in practice, because there are factors involved which he has not considered and which may be relatively great.

Mr. C. J. Reed: My experience with this is, that the actual facts agree almost exactly with the figures which Professor Richards has given in this particular case, except that I found experimentally that there are only .25 volt, instead of .27, required to evolve hydrogen under those conditions; and I think that may be accounted for by the fact that Professor Richards used a rather strong current, in order to get an evolution of hydrogen before the copper had all been deposited. With a strong current, of course, it would require undoubtedly two or three hundredths more difference of potential on account of the resistance of the electrolyte.

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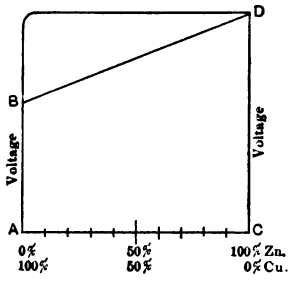
Dr. Richards' conclusions indicate, as Mr. Hering has interpreted it, that the cell would itself act as a battery, and, therefore if these results are true the process of refining copper would not require any energy; in other words, an impure anode connected with a pure copper cathode would cause the copper to refine itself. It is, however, very evident that, since the anode has to be immersed in a solution of a copper salt, this current would take place through local short-circuits and, consequently, the copper would, as Mr. Hering has said, be deposited on the anode instead of on the cathode; because that would be the line of least resistance, and practically it would not work as an automatic method of purification.

Dr. R. Gahl: I should like to represent graphically what the results of Professor Richards mean.



If AB represents the voltage for the deposition of one metal, say for example, copper, and CD represents the voltage for the deposition of another metal, say zinc (of course these values must not be calculated necessarily from the heat of reaction, but can be taken from real observation), then Dr. Richards claims that the intermediate voltages (that means the voltages required for depositing both metals together) can be found very easily by connecting the points B and D by a straight line. This contradicts the results which can be derived by an application of the osmotic theory of electromotive forces. The osmotic theory shows that it is indeed possible to electrolyze zinc out of a solution containing copper at a lower voltage than the electrolysis of zinc would require if no copper is deposited at the same time, but this difference is very small, practically zero, if no chemical compound of

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the two metals, but only a solid solution, is formed. The curve connecting B and D is meant to show what voltages may be expected from an application of the osmotic theory. If a chemical compound is formed, however, and I think copper and zinc form chemical compounds, the free energy for the formation of such an alloy must be accounted for. In such a case the voltage for depositing the two metals together will be depressed and the real curve of the voltages will not follow the curve in the sketch, but may be considerably lower. But there is no reason that the real curve should follow the straight line.

MR. REED: According to my experience, the curve is practically the straight line. As soon as the quantity of copper begins to get very small the voltage begins to gradually increase, and goes up until there is no copper left. Then you have the voltage required for the hydrogen. We could not keep the current flowing at practically the same voltage until the copper is all gone.

MR. ADDICKS: It would seem to me that the curve drawn by Dr. Gahl would require that even though we had a foul solution we would get a perfectly pure deposit, unless there was a large change of voltage in the cell. We do plate out soluble impurities in the refining of copper, even though the proportion be minute; and yet the voltage of the cell may be so slightly above the normal that we would hardly notice it.

DR. GAHL: Of course in the case of copper and zinc the curve I have drawn is not right, because copper and zinc form chemical compounds, as far as I know, and the curve observed in practice may be much nearer to Dr. Richards' curve than to the other one. But I could not think of another case where it was certain that no chemical reaction between the two metals deposited took place, and therefore figured with copper and zinc.

MR. REED: I think in this case no zinc is deposited whatever, but only at first copper and then hydrogen.

DR. GAHL: You spoke about something else than I did. I only used copper and zinc as an example to represent two metals which are deposited simultaneously without other cathodic reactions occurring in the same time. This example is not very well chosen for the reason I referred to before. Besides this, the development of hydrogen which will start when no copper is left in solution and the process going on consists only in deposition

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of zinc, is another reason that it does not illustrate very well the simplest case of electro-deposition, *i. e.*, electro-deposition of two metals, which do not form chemical compounds and are deposited without another cathodic reaction going on. All this shows distinctly that it is not easy to calculate the electromotive forces for practical processes, as very many things have to be accounted for. What I wished to state, is, that for the simplest case possible, the straight line which Professor Richards draws is not right, and must be replaced by another curve, which may be derived by applying the osmotic theory of electromotive forces.

MR. HERING: Dr. Gahl remarked that one cannot deposit zinc without some evolution of hydrogen. He is not quite right. I have myself deposited zinc in practice without the slightest evolution of hydrogen. I am not in position now to describe the method; but it can be done. I have gotten 94 per cent. of the zinc out of a solution of zinc sulphate without any evolution of hydrogen, the hydrogen did not begin to be evolved until the zinc was almost entirely extracted. Among the factors that I think Dr. Richards should include in his calculation is the composition energy of the formation of alloys.

DR. J. W. RICHARDS: I was pleased to hear from Mr. Addicks, because of his great experience in refining copper; and I had particularly in mind, in refining copper, the solution of the iron and nickel at the anode and the possibility of depositing those at the cathode with an almost inappreciable increase of voltage in the bath. It was for that reason that I took this as a suppositious case of a compound anode, and it must be clear to everyone that when in actual practice these things are being dissolved, you must get then the energy of their solution added to the circuit. If you do get some of those simultaneously deposited with the copper at the cathode, then there is also some absorption of energy taken from the circuit to do that. In that connection, Mr. Mott and Mr. Hering raise the point of there being local action. The calculations, of course, would not apply to the case of the zinc or iron dissolved by local action. Whatever is dissolved by local action forms a closed circuit, which does not affect the voltage of the main circuit. So that while it is undoubtedly true that some of these may be dissolved by local action, yet in the actual refining of copper I am sure that the larger part of the impurities dissolved

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which come into solution are dissolved by the main action of the current, and not by the local action. You could not, at least, cite local action to explain the solution of the copper-nickel anode in Mr. Brown's process, where the anode is 50 per cent. copper and 50 per cent. nickel. You could not explain the 50 per cent. nickel by local action. When Mr. Hering raises the point that the calculated voltages are so small in this case that they would be obscured by other items, it is certain that numerically in the case of copper they may be smaller than some of the other items in the case; but in the case of copper and nickel being dissolved the voltage corresponds to something like .45 volt; so that it is a very large item in practical operation, possibly one of the principal items in the running of the Brown cell. I distinctly stated in my paper that I had not complicated the reactions by taking into the calculation the heat of formation of the copper-nickel alloy, or of the alloying of these metals with the impure copper, because that was not known. If they were known, they could be simply added to or subtracted from the calculation, and that would make it more accurate. I was considering the calculation of the chemical work done, independent of the breaking up or the formation of an alloy, because the heat of the latter in general is not known; and also with regard to the Caspari effect, that is, the overvoltage which is needed to start the hydrogen evolving, I have not taken that into the calculation.

My paper is not altogether a theoretical paper, without any practical basis, as Mr. Hering suggested; because I have, in common with Mr. Reed, observed this rise of voltage as the last of the metals, say copper, in solution is being plated out and the hydrogen begins to evolve; and I think it was that which led me to make the calculations as to the amount of work being done by the current in the interim. We must distinguish carefully between the deposit of the metals consecutively and depositing them simultaneously. In the practice of the cases which I have wished my calculations to meet, those cases where cathodic reactions are going on simultaneously, a solution of copper occurring continuously at the anode, it is not to a case where you have the depositing first of one metal and then afterwards the depositing of the other. I used that only to show that there were intermediate states; and in practice it is these intermediate states which are the

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continuous states. That point explains, I think, Dr. Gahl's objection, that if I am plating out copper and zinc I would find the voltage steady until nearly all the copper was out and then it would go up suddenly when the alloys commenced to be deposited. I have not made the measurements with copper and zinc, but with copper and hydrogen I know that the voltage goes up very nearly linearly and steadily from the voltage required to deposit copper to that required to deposit hydrogen; and these intermediate stages will represent the practical cases where hydrogen is continuously evolved and copper simultaneously deposited.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 8, 1904, Vice-President Carhart in the Chair.

MOLECULAR CONDUCTIVITY.

By C. J. Reed

Electrical conductivity is a property of matter, which, like transparency, diathermacy, magnetic permeability and heat-conductivity, can be measured or compared in different substances only by employing a unit in which there is a definite section, across which the flux is measured and a definite length in the direction of the flux. Units of this kind must be defined by certain relations of form in which the ratio of length to cross-section is a fixed ratio.

We could not, for example, compare the conductivities of iron and copper by measuring the conductance of a pound of iron and the conductance of a pound of copper, without any reference to form or dimensions. What is true of a pound of iron or copper is equally true of a gram-molecule. We may measure the conductance of a pound or gram-molecule of iron or copper or salt or electrolyte without reducing the measurement to a common unit, but this would not be a measure of the conductivity, that is, of the property of matter in virtue of which it conducts electrically. Of course, the actual measurements for comparison may be made on conductors of any form or size provided the form is reducible to the common unit, but a comparison cannot be made until after the reduction to a common unit is made.

Let us assume, for convenience of illustration, that our unit for the comparison of conductivities is a rectangular cylinder or prism having a length of 1 centimeter and a section of 1 square centimeter. Let us assume that such a prism of silver has a certain conductance when measured between its opposite parallel ends. This conductance we may call unity. This may also be taken as the *conductivity* of silver. Let us now suppose the prism of silver to expand uniformly and to retain its original form, so that we have a prism 2 centimeters long and of 4 square centimeters cross-section.

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If, in this expanding process, there is no change in the conducting property of the silver, the conductance between the opposite ends before expansion will not be the same as after expansion, because of the alteration in the dimensions of the unit, although there is no change in the form. The conductance after expansion would be $\frac{4}{2} = 2$ times the conductance before expansion. In other words, before making comparisons we must reduce our measurements to units of a standard size.

Suppose now, instead of allowing the prism to expand uniformly in all directions, we confine its ends between two immovable parallel walls 1 centimeter apart, and allow the expanded mass to spread out laterally by increasing its cross-section. We should now have, with the same expansion, a length of 1 centimeter and a cross-section of 8 square centimeters. The conductance after expansion would be eight times the conductance before expansion, provided, as before, that there is no change in the conductivity. If, therefore, we wish to determine or compare the electrical conductivities of the silver before and after expansion, we must divide the second measurement by 8, the increase in cross-section. To say that the conductivity of the substance has increased by expansion, merely because the conductance of the expanded and flattened form has increased, would be nonsense, if by conductivity we refer to any property of matter.

There are two methods or processes by which an expansion of matter may be supposed to take place.

In one process the particles of the substance simply recede to a greater distance from one another without any foreign substance intervening or being injected between the molecules. This would be a process of true expansion, such as would be generally produced by an increase of temperature.

In the other process the molecules of the expanding substance are separated to greater distances by the injection between them of molecules of other substances. This process is more properly called dilution than expansion. Dilution could be produced in the case of our silver prism by melting and alloying the silver with any desired quantity of lead or other metal with which it would form a homogeneous alloy. As a matter of fact, such alloys are generally homogeneous only in the liquid state; but, for the purpose of illustration, we may suppose that measurements are made

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of the molten homogeneous mixture. And we may suppose that in this state, as in an ordinary aqueous solution, the various kinds of molecules are uniformly distributed.

To compare the electrical conductivities of a diluted substance in different degrees of dilution, whether it be an aqueous or fused substance, is a different problem from comparing the conductivities of an expanded substance in different degrees of expansion. In the case of diluted substances we must not only reduce our measurements of conductance to a standard unit as to form and dimensions, but we must also determine to what extent the conductivity of the mixture is due to the diluted substance and to what extent it is due to the solvent or diluent. If we were to measure the conductance of a certain cube of silver between opposite faces, then fuse the silver with 200 times its volume of lead and measure the conductance of the resulting alloy between faces having 200 times the area of the original faces, we could not conclude from this that the conductance so measured represents the molecular *conductivities of the silver* in the two conditions of concentration, or any other conductivities. I do not believe anyone except an electrochemist would like to be accused of such a procedure. What is measured in this case is not conductivities, but conductances, and not conductances of the same thing in two states of concentration, but the conductances of two entirely different substances, silver and a mixture of silver and lead.

But this is exactly what is done by the electrochemist, or physicist who talks about the "molecular conductivities" of solutions in different degrees of dilution. The conductance of a litre of solution, containing a gram-molecule, is measured in the form of a flat prism 1 centimeter thick and having a cross-section of 10 square decimeters. This conductance is taken as the "conductivity" of the normal solution. Dilutions are made by adding water and spreading out the increased volume, whatever it may be, into a flat plate of the same thickness, 1 centimeter, and increasing the cross-section in proportion to the increased volume. The conductances of these extended volumes measured between the parallel sides are called "molecular conductivities" merely because the measured volumes contain a gram-molecule of the solute. The assumption is made general (probably for convenience), that the only substance which takes part in the conduction is the substance

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whose so-called "molecular conductivity" (conductance) it is desired to measure.

The fact has been experimentally established beyond question that water does take part, and an important part, in the conduction of at least some aqueous solutions, and there is no experimental evidence in regard to any particular aqueous solution, showing that water does not take part as a conductor. The purest water obtainable has an exceedingly low conductivity, and it is common to speak of it as a non-conductor. The same is true of pure hydrogen chloride. If we add a drop of water to a litre of pure HCl or a drop of HCl to a litre of pure water, both mixtures become conductors. The conductivity of the water increases by increasing the amount of HCl added. So also does the conductivity of the HCl increase by adding more water, until a certain composition has been reached, when the conductivity of the mixture is at a maximum.

If these facts are evidence of anything in regard to the conductivity of the HCl and H_2O in solution, they are evidence that neither substance is a conductor in the pure state and that the conductivity of the solution is dependent upon the presence of both. What ground have we, therefore, for the assumption that either the conductivity or the conductance of dilute HCl is due entirely to the HCl and not at all to the H_2O? If the solvent takes part in the conduction in the case of solutions of HCl, how do we know it is not so in all other cases? There is no proof to the contrary. In this connection the experiments of H. E. Patten on "The Influence of the Solvent in Electrolytic Conduction,"* are instructive. The general conclusion to be drawn from his results is that the conductivity of an electrolyte is a maximum with a particular proportion of solvent and solute, and that reducing the proportion of either the solvent or the solute reduces the conductivity.

The harm which results from the use of, and from deductions based upon quantities like "molecular conductivity," which have no real existence, would be less if the distinctive term were always used. But some of the physicists who have frequent use for "molecular conductivities," and have, consequently, become very

* Journal of Phys. Chem. 6, Nov. (1902).

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familiar with the subject, have gone so far as to abbreviate the term to "conductivity," omitting the word "molecular." We frequently read, for example, such sentences as the following, taken from Prof. H. C. Jones' "Theory of Electrolytic Discussion." He says, on page 142, "It is well known that the power of solutions of electrolytes to conduct the current increases with dilution." Such a statement is absolutely false and gives to the student an entirely erroneous conception. The fact is that the power of aqueous solutions of electrolytes to conduct the current in general decreases rapidly with dilution. But in the sentence quoted above, Professor Jones means "molecular conductivity," when he says "power to conduct the current." There is a very great difference between the "power to conduct the current" and "molecular conductivity." The former is a property of matter; the latter is merely a number representing a product obtained by multiplying the intensity of this property by a variable factor. Although Professor Jones means "molecular conductivity" in his statement, he reasons from the words "power to conduct the current," which refers to the property of matter. It is only by reasoning from this sense of the expression that he could arrive at his conclusions, namely, that there is an increased number of ions in dilute solutions. The increase in "molecular conductivity" with increased dilution, does not require any increase in "conducting power," and, consequently, does not require any increase in the number of ions. In fact the so-called "molecular conductivity" does not increase with dilution as rapidly as it should increase, even for a constant conducting power; that is, for a constant number of ions. The conducting power and, therefore, the number of ions rapidly diminishes with dilution, but the change in the form and dimensions of the conducting mass caused by increasing dilution, according to the method used in "molecular conductivity" measurements, results in measurements of *conductance* which slowly increase with dilution.

Professor Jones is not alone in this careless use of the word "conductivity" when "molecular conductivity," or more properly speaking, "molecular conductance" is meant. Professor Arrhenius in his "Text-book of Electrochemistry," (English edition), uses the word "conductivity" on page 127 and elsewhere, meaning "molecular conductance." He says, for example: "If we start,

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for instance, with a 0.01 normal solution of zinc sulphate, which contains 1.61 grams of $ZnSO_4$ in a litre, then on dilution to double the volume, the resistance is reduced by 11.7 per cent., or the conductivity increased by about 13.3 per cent. ($1.132 = \frac{1}{0.883}$) If the solution be diluted to four times its original volume, so that the level in the trough is pp_1, the conductivity is increased by no less than 26.3 per cent. To explain this phenomenon it must be assumed that the number of zinc and sulphate ions has been increased by 13.2 and 26.3 per cent. respectively by the dilutions. We must therefore conclude that *the quantity of the ions, and consequently also the degree of electrolytic dissociation, increases with dilution.*"

Here Professor Arrhenius has not only used the word "conductivity" where he means "molecular conductance," but he has drawn conclusions which could only follow if he had actually meant "conductivity." In other words, his conclusion is based upon an increase in actual "conductivity" of the solution when there is no such increase. His conclusion is not warranted by a mere increase in "molecular conductivity."

Professor Nernst, in his admirable treatise on "Theoretical Chemistry," page 440 (English edition), makes the same mistake and draws the same erroneous conclusion. He says, "*and therefore the conductivity of an acid in equivalent concentration corresponds, at least approximately, to the degree of its electrolytic dissociation, i. e., to its strength.*

"On the whole, the order of succession as arranged in accordance with the conductivities, is identical with the order of succession as shown by their acids in their specific reactions. The recognition by Arrhenius and Oswald (in 1885) of this remarkable parallelism was an important event, for it amounted to the discovery of electrolytic dissociation."

From this we see that, on the authority of Professor Nernst, so important an event as the discovery of electrolytic dissociation by Arrhenius and Oswald depended upon the error of confusing "conductivity" a property of matter, with "molecular conductivities," mere numbers obtained by the use of arbitrarily-chosen factors.

I would call attention to the fact that this same confusion pre-

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vails in the works of almost all writers on electrochemistry such as Ostwald, Le Blanc, Luepke.

In view of the facts it seems to me that the term "molecular conductivity" and that all theoretical deductions based on investigations of "molecular conductivities" of different degrees of dilution have no physical significance.

DISCUSSION.

MR. CARL HERING: I am very glad to see that Mr. Reed brought out this important distinction between the words "conductance" and "conductivity." It seems to be necessary to call attention to this, as he has done, because these words seem to have been used quite incorrectly, even by distinguished writers. There ought not to be such a misunderstanding concerning those words. "Conductance" corresponds exactly to "resistance," and can apply only to a body of definite form, length and cross-section; while "conductivity" corresponds to "resistivity," and is a property of matter entirely independent of shape or form or quantity, just as Mr. Reed has stated it. Conductivity is specific conductance; such a thing as "specific conductivity" is absurd; it should be either specific conductance, or conductivity, but never specific conductivity; yet we find that term specific conductivity used frequently. Specific resistivity is equally absurd; it is either resistivity or specific resistance, which two terms mean the same thing. I heartily agree with Mr. Reed in all he says about the definitions and the meanings of those two terms.

DR. E. F. ROEBER: The general statements of Mr. Reed in the first part of his paper will probably be accepted by everybody. Conductivity is universally defined by the relation

$$(1) \qquad \text{conductance} = \text{conductivity} \times \frac{\text{cross-section}}{\text{length}}$$

the cross-section and the length referring to a cylinder of uniform cross-section and uniform composition throughout, through which the current flows in the direction of the length. What we measure in practice is always a conductance; from it we calculate the

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conductivity by equation (1). Concerning molecular conductivity, however, I cannot agree with Mr. Reed's arguments. At the starting point of his criticisms, the analogy of the lead-silver alloy, is, in my opinion, most unfortunate and far from representing "exactly what is done by the electrochemist," for the following reason: The term molecular conductivity was introduced by Kohlrausch in order to describe concisely his measurements of dilute aqueous solutions; the introduction of this term follows with absolute consequence from the mechanical model of travelling ions, together with Kohlrausch's empirical law of ionic mobilities. What justification is there then in the analogy of the lead-silver alloy to which neither Faraday's law—the foundation of the model of traveling ions—nor Kohlrausch's mobilities can be applied?

Everybody has a perfect right to express his disbelief in the correctness of the electrolytic dissociation theory. But the only way to prove it to be either right or wrong, is to draw all conclusions which can be drawn from it with strict consequence, and then to compare them with the facts. This is the only legitimate way of arguing about a scientific theory. Now, first, I will not assume Arrhenius' theory, but base the argument simply on the model of traveling ions—that is, the illustration of Faraday's law—and on Kohlrausch's law of ionic mobilities. What follows from these assumptions?

Let us consider a rectangular cylinder of the length l and cross-section q, containing a dilute aqueous solution of a salt; the current flows in the direction l through the solution, and we assume that there is the same current density at any point of any cross-section. The conductance of this cylinder is, according to Ohm's law, equal to the ampères passing through the total cross-section, divided by the difference of potential $\varphi_2 - \varphi_1$ at the two ends of the cylinder. Instead of the number of ampères we may say number of coulombs passing through any cross-section in a time interval t, divided by this time t. If we now use the model of traveling ions, the number of coulombs passing through any cross-section in the time interval t is equal to the sum of the number x of positive monovalent gram-ions passing through this cross-section in the time t towards the cathode, and of the number of negative monovalent gram-ions y passing through the same cross-section in the same time towards the anode. (Here I purposely

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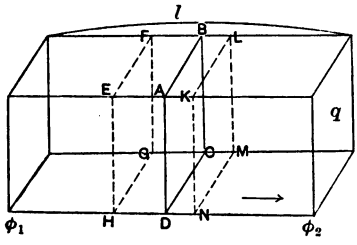
neglect the constant factor 96,540. In this calculation I purposely leave out such constant factors which only depend on the units chosen. Everybody can easily put them in, if he wants to do so. I also assume we have only to do with monovalent ions.)

We have now to calculate x and y. The cross-section to which we refer, may be ABCD in the adjoining diagram; x positive ions pass through it from left to right, and y negative ions from



right to left in the time interval t. At the beginning of this time interval these x positive ions are in a cylindrical volume, between the cross-sections EFGH and ABCD, while the y negative ions are in a cylindrical volume between the cross-sections ABCD and KLMN. To calculate these two volumes we need to calculate only the lengths EA and AK. We find these lengths by means of the consideration that all the positive ions which are in the cross-section EFGH at the beginning of the time interval t will arrive at the end of this time interval just at the cross-section ABCD. Now, each of these ions travels with a speed which, according to Kohlrausch's law, equals its mobility u multiplied by the electric driving force, expressed as the drop of potential per unit length. The drop of potential per unit length is $\frac{\varphi_2 - \varphi_1}{l}$. Hence the speed of each positive ion is $\frac{u(\varphi_2 - \varphi_1)}{l}$, therefore the length EA, i. e., the distance through which each positive ion travels at this constant speed in the time t, is $\frac{tu(\varphi_2 - \varphi_1)}{l}$. In the same way it can be shown that $AK = \frac{(tv\,\varphi_2 - \varphi_1)}{l}$ where v is the mobility of the negative ions. The volume between the cross-sections EFGH and

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ABCD is therefore $\frac{tuq(\varphi_2-\varphi_1)}{l}$ and the volume between the cross-sections ABCD and KLMN is $\frac{tvq(\varphi_2-\varphi_1)}{l}$. The concentration of our aqueous solution may be c (gram-molecules of dissolved salt per unit of volume), then we may *either* assume that all gram-molecules of the dissolved salt participate equally in the conduction of the current, *i. e.,* are ions; *or,* according to Arrhenius, that only a certain number of the same is ionized; in the latter case, we may write i for the ratio of the number of ionized molecules to the total number of dissolved molecules. In the first case i is unity. We therefore render our calculation general, if we introduce i into it; we can then later decide whether we want to make it unity or not. In the latter case we would assume Arrhenius' hypothesis, in the former case we would not.

We can now write down the values of the above-defined numbers x and y of positive and negative ions, respectively, since these numbers are equal to volume multiplied by ionic concentration. We get

$$x = \frac{tuqic(\varphi_2 - \varphi_1)}{l}$$

and

$$y = \frac{tvqic(\varphi_2 - \varphi_1)}{l}$$

Hence, since we found above that the conductance of our whole cylinder under consideration is $(x + y)$ divided by $(\varphi_2 - \varphi_1)\ t$, we have now

$$(2) \qquad \text{conductance} = \frac{(u + v)\ qic}{l}$$

By combining equations (1) and (2) we get

$$(3) \qquad \text{conductivity} = (u + v)\ ic$$

By dividing both sides by c (concentration in gram-molecules), we get at the left hand the ratio of conductivity to concentration and call this ratio *molecular conductivity.* This is the definition of molecular conductivity, and we have

$$(4) \qquad \text{molecular conductivity} = (u + v)\ i$$

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This equation follows with absolute consequence from the ionic theory in combination with Faraday's law. But has it a physical significance? This question must be answered in connection with the experimental fact that the molecular conductivity, as defined above, increases with increasing dilution. We may consider the equation (4) from two different points of view. First from the old point of view that all particles of the dissolved salt participate equally in the conduction of the current. Then $i = 1$ for any degree of dilution, and since the molecular conductivity increases with dilution, we must assume that the mobilities u and v also increase with dilution. The physical significance of equation (4) then rests in the experimental fact that in an "infinitely dilute" solution u and v have distinct values, u only depending on the chemical nature of the cation alone, v only depending on the chemical nature of the anion alone. For instance, the mobility u of H ions is the same for all acids, the mobility v of Cl ions is the same for all chlorides. This is an experimental fact which has surely physical significance. Therefore, the molecular conductivity, being the sum of u and v, has also physical significance.

On the other hand, if we assume Arrhenius' hypothesis that only a certain number of the molecules of the dissolved salt are ionized and that only this ionized part is active in the transference of the current and that the mobilities u and v are independent of the dilution, then in equation (4) $u + v$ is a constant quantity, and it follows that since the molecular conductivity increases with dilution, i also increases. For "infinite dilution" the ionization is complete, hence the molecular conductivity $= u + v$; for any other degree of dilution the molecular conductivity is $i(u + v)$; $u + v$ is a constant quantity; hence, the value i—*i. e.*, the degree of ionization for a given dilution—is directly given by the ratio of the molecular conductivity at this dilution to the molecular conductivity at infinite dilution. This is Arrhenius' equation. This is the sense of the statements of Jones, Nernst and Arrhenius, which Mr. Reed has attacked. There is absolutely no flaw in this argument, provided the premises are granted. With regard to this point, there is absolutely no confusion among the advocates of the dissociation theory, as Mr. Reed would make us believe. Nobody has ever claimed that a liter of a 0.001 normal solution contains more ions than a liter of a 0.01 normal solution; what

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has been claimed is that the degree of ionization is greater in the former than in the latter, or in other words, that if you take a liter of 0.01 normal solution and add pure water, the number of ions in the total volume increases with the volume.

Now concerning the usual method of measuring the molecular conductivity, attacked on the third page of Mr. Reed's paper. I agree with Mr. Reed that what we measure is a conductance. But molecular conductivity is defined as conductivity divided by concentration, or what is the same, as conductance multiplied by $\frac{l}{q}$ divided by concentration; hence, conductance = molecular conductivity $\times \frac{q}{l} \times$ concentration =

$$\text{molecular conductivity} \times \frac{\text{number of dissolved gram-molecules.}}{l^2}$$

This equation is correct whatever may be the dimensions of the cylindrical body, whose conductance is under consideration and whatever may be the number of gram-molecules dissolved in it. What is done in the method, attacked by Mr. Reed, is that l is made unity and that the number of the dissolved gram-molecules is also made unity. Hence the second term at the right hand becomes unity, and while we measure the conductance, the numerical value found for this conductance gives us directly the numerical value for the molecular conductivity. Thus, the method is correct. With respect to dimensions, conductance, conductivity and molecular conductivity are all different from each other.

Finally, I will drop the whole ionic theory, so as to be able to approach somewhat Mr. Reed's example of the lead-silver alloy. If we have a constant weight of a pure substance and add to it variable quantities of another substance, for instance, an alloy of a constant weight of lead with variable quantities of silver, and if the variable concentration of the addition "dissolved" in the lead is called x, then the conductivity $f(x)$ of the alloy will be a function of the concentration x, and we can develop it in a series

$$f(x) = f(o) + \frac{x}{1}\frac{df(o)}{dx} + \frac{x^2}{1 \times 2}\frac{d^2 f(o)}{d x^2} + \ldots$$

where $f(o)$ is the conductivity of the pure solvent (lead). Whether such a series, even if mathematically converging, would

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have any practical value in general, I don't know, but I doubt it. But for the special case that we prepare a series of such alloys containing less and less silver, corresponding to more and more dilute solutions, we see that the less the amount of silver compared with lead, the more we will be able to neglect all terms at the right hand except the first two, and we get

$$f(x) = f(o) + x \frac{df(o)}{dx}$$

We then get

$$\frac{df(o)}{dx} = \frac{f(x) - f(o)}{x}.$$

This is the general analogy to molecular conductivity. In the case of water as solvent, if we assume for a moment pure water to be an absolute non-conductor, we get

$$f(o) = o, \text{ and } \frac{df(o)}{dx} = \frac{f(x)}{x}$$

equal to conductivity divided by concentration which is the definition of molecular conductivity. But if we go further and further down in concentration, it would be wrong to neglect the conductivity of pure water, $f(o)$, then we must use the general equation

$$\frac{df(o)}{dx} = \frac{f(x) - f(o)}{x},$$

i. e., we must substract the conductivity of the pure water from the conductivity of the solution. This is what Kohlrausch has done in working out his results.

We could now treat just as well alloys of lead and silver, containing small amounts of silver, and by working out the results of the measurements, we could see how far we have to go down in the concentration, in order to be justified in considering only the first two terms of our series. This would be useful work, but I don't think that we would speak of $\frac{df(o)}{dx}$ as molecular conductivity until we would find that this term has a similar distinct physical significance as in the case of dilute aqueous solutions. In the latter case the physical significance of molecular conductivity is, as I tried to show, most intimately connected with Faraday's law, Kohlrausch's law and Arrhenius' degree of ionization. If we

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could build up *experimentally* a theory of similar significance for the use of metallic alloys, it would, in my opinion, represent a most important advance in our knowledge of the conduction of the electric current through "conductors of the first class."

DR. R. GAHL: I am sure that Mr. Reed's criticism of the dissociation theory is chiefly due to a misunderstanding of certain points of this theory. By a private discussion with him, I think, that one of these points was brought out.

The definition of molecular conductivity according to text-books is expressed by the formula:

$$\triangle = \frac{x}{y}$$

That means molecular conductivity is conductivity divided by concentration.

Now, Mr. Reed says, if you determine the molecular conductivity from this formula for a substance dissolved in an infinite amount of water, so that the solution is not different from water, you get an infinitely high value for the molecular conductivity of this substance. Indeed, x is then the conductivity of pure water, y is zero and $\triangle$ the molecular conductivity is infinitely great.

Mr. Reed is perfectly right in saying that this has no sense, and that therefore the formula, or a picture describing this formula, is not correct. But it is easy to make this formula quite correct by subtracting the conductivity of pure water. The formula is then:

$$\triangle = \frac{x - xw}{y}$$

and in this form has a well-defined limit for an infinitely diluted solution, the molecular conductivity for infinitely dilute solutions, which is fundamental to the dissociation theory.

I said before, that the first definition is not correct. Nevertheless for almost all cases both formulas would give practically the same result, as conductivity of water is so extremely small. As a matter of fact, for all measurements the second formula is used, as water always has a certain negligible conductivity on account of impurities.

So I think, it is safe to state, that though the formula generally given in the text-books for molecular conductivity does not hold

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for infinitely dilute solutions, all measurements on which this part of the dissociation theory is based took account of this fact and are perfectly right.

DR. J. W. RICHARDS: Just one remark as to a point which has been brought up. In the case of measuring the conductivities of very dilute solutions, Kohlrausch calculates what he calls molecular conductivity from his measurements of conductance, and subtracts from these the conductivity of the water, or rather the conductance of the water which is used. Ever since first reading those experiments it shook my faith in the accuracy of the determinations of limiting molecular conductivity. I do not believe that the conductance of the water should be subtracted from the conductance of the solution to get the molecular conductivity of the dissolved salt. It seems to me assuming an additive property of the conductance of the solution for which there was no justification.

DR. GAHL: The assumption to which Professor Richards refers is certainly made, but it is justified by experience, which has shown, that for dilute solutions conductivity is an additive quality unless some chemical reaction takes place between the substances.

MR. C. J. REED: My statements are on the definition of molecular conductivity given in authoritative books on electrochemistry, viz., molecular conductivity equals conductivity multiplied by volume or conductivity divided by concentration. Dr. Roeber has given you an entirely different definition. If we accept his definition of molecular conductivity, all of my statements are, nevertheless, true. Dr. Roeber has not brought forth anything to controvert it. If molecular conductivity is what he has here given, it is something entirely different from the molecular conductivity defined by Arrhenius, but even this molecular conductivity has not any physical significance. According to Arrhenius and all the other authors, molecular conductivity is physical conductance of one unit multiplied by the volume occupied by an arbitrarily chosen quantity of solute, viz., a gram-molecule. In speaking of the molecular conductivity of a substance (the conductance of a gram-molecule at different degrees of dilution) the molecular conductivity is defined as the "conductivity of that diluted solution multiplied by the volume or divided by the concentration."

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Dr. Roeber's molecular conductivity is purely a mathematical quantity based upon an assumed quality of matter which has mathematical properties instead of chemical or physical properties. It assumes, for instance, because the physical conductivity of the molecules of water in the pure state is zero (or so small as to be considered zero), that this value may be used in a mathematical formula to determine the effect of the same molecules in various mixtures or dilutions with other substances. From this he obtains a mathematical "conductivity," but it has no physical significance in the sense of representing any quality or property of matter.

MR. HERING: It cannot be the same thing, because concentration is a function of mass and volume.

MR. REED: They are the same thing, and are so stated by the text-books. For example, suppose we have a normal concentration and dilute it to one-half normal concentration, then we distribute the same gram-molecules through 2 litres. We double the volume; that is, we divide the concentration by two, or make the concentration one-half. I am simply taking the statements as given by all the authorities on this subject.

COL. S. REBER: I quite agree with Mr. Reed's statements, and I think that Dr. Roeber has overlooked the main point. What Mr. Reed says is this: that the particular equation under discussion has no physical significance, and I thoroughly agree with Mr. Reed that no physical quantity is represented by it.

DR. ROEBER: I would recognize the significance of the criticism of Colonel Reber, were it not for the fact that the values of i in the formula given by me, when calculated from conductivity measurements, agree for *dilute* solutions with the values of the degree of ionization, calculated from the variations of the freezing point and boiling point on the basis of the dissociation theory. The great value of Arrhenius' hypothesis is that it connects fields which were formerly disconnected.

MR. HERING: My contention is that there has been altogether too much looseness in the use of terms in literature, which I think is proved by this controversy.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 8, 1904, President Richards in the Chair.

THE ECONOMIC BALANCE IN ELECTROLYTIC COPPER REFINING.

By Lawrence Addicks.

In discussing Dr. Bancroft's paper at the last meeting of this Society, on the effect of current density and temperature on the cost of electrolytic copper refining, I objected to the drawing of conclusions as to the most economical density, etc., on the ground that an insufficient number of conditions were considered. Probably few persons not in daily contact with such work realize the close interdependence of relations which forms what I have termed the economic balance. It is the purpose of this paper to indicate, in a general way, these relations and their bearing on the cost of production.

The problem may be separated into three variables—tank resistance, age of electrodes and current density. They can be best considered in the order given.

Tank resistance is made up of metallic conductors, contacts, anode slimes, counter e. m. f., electrolyte and a negative quantity due to imperfect efficiency. The metallic conductors consist of the leads from the generators, the circuit bars and rods supporting the electrodes, and the electrodes themselves. The chief item here is in the circuit bars running from tank to tank. This resistance can be lowered either by increasing the section of the bars, or by increasing the number of tanks abreast. The first method is limited by the cost of the copper required; the second involves a consideration of the increased labor cost due to inaccessibility, the loss in output caused by the increased number of tanks which have to be cut out of electrical service when changing electrodes or removing slimes, and, finally, the saving in first cost of plant.

The loss from contacts depends on their number, the weight bearing down and the condition in which they are maintained. The number depends upon whether or not the anode is provided

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with supporting lugs—if so, the weight of scrap made is proportionately increased. The average weight depends on the age of electrodes. The condition is governed by the labor expended in shining, and by the exposure to moisture and fumes, or, in other words, by the temperature of electrolyte.

The resistance due to slimes adhering to the anode is a very variable one, and depends, of course, upon the thickness of the layer allowed to form upon its surface. Very impure anodes and a high current density give great trouble.

Counter electromotive force is due chiefly to the difference in concentration at the electrodes. Circulation tends to check this, but no amount of circulation will obliterate it.

We come now to the resistance of the electrolyte itself. This depends upon composition and temperature. Resistance varies greatly with changes in the chemical composition. In deciding upon the composition to be maintained, we are governed largely by the impurities in the anode copper. Arsenic is the most difficult to handle. With small quantities of arsenic present in the anode the electrolyte may be maintained reasonably pure without a special purifying process, the quantity of arsenic slimed balancing that introduced at the anode before the per cent. arsenic in the solution reaches a troublesome amount. A high current density magnifies these difficulties. The amount of copper carried as sulphate by the electrolyte must be sufficiently in excess of the arsenic to insure satisfactory purity in the cathode at the tank voltages existing. In free acid contents we are also limited by the decomposition point—a percentage at which electrolysis of water commences with resulting polarization.

The temperature coefficient is large, and we have a balance to strike between power saving, cost of heating, increased contact losses, and increased cost of keeping the copper contents of the electrolyte down to the required figure. When considering the saving in power from heating the electrolyte, we must not lose sight of the fact that we are dealing with but part of the total resistance of the circuit. Starting at the generator terminals, if we have an electrolyte of low resistance and an anode running high in impurities, the liquid resistance may not greatly exceed 50 per cent. of the total. With a different set of conditions it may be 80 per cent., or more, but in any case this factor must be

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reckoned with. The spacing of the electrodes, or, in other words, the thickness of the liquid column, has a great deal to do with tank resistance; it must be considered in connection with age of electrodes and current efficiency.

A diminishing current efficiency forms an effective, but somewhat expensive, way of arriving at a low tank resistance. It must be remembered, however, when deciding upon the efficiency which it pays to maintain that the loss in output from this cause is accompanied by a certain diminution in total power charges.

Turning now to the question of age of electrodes, much depends upon whether or not we are charged with interest on the metals tied up in the process. If so, we will use a lighter anode than otherwise, though the question of current density must be taken up at the same time. A heavy anode reduces the percentage of scrap and the handling charges, as it is the number of electrodes rather than the pounds of electrodes that figure in tank-room handling. The heavier the average weight during life the better the contacts. With the cathodes smoothness of deposition is the governing factor, as upon it depends the current efficiency. The smoothness depends upon age, electrode spacing, current density, circulation and composition of electrolyte. On the other hand, as the age decreases, handling charges and the cost of stripping starting sheets runs up. As a partial offset to the increased number of stripping tanks required per hundred depositing tanks, we have the very high current efficiency obtained in these tanks due to the rigidity and low age of the cathodes.

Finally from the standpoint of current density the problem becomes largely one of output. With any given plant the simplest way to increase the output is to raise the current density. Even our largest plants still have a respectable proportion of fixed charges, and the distribution of these over a larger tonnage is always an attractive proposition. If interest charges are involved, we gain here as well. With a rising density, however, we are met by a rapidly-increasing power cost and a roughening of the deposit. The small counter e. m. f. present keeps the power needed per tank from increasing quite as the square of the current density, but it approaches this ratio. The rougher cathodes require a readjustment of several of the conditions previously outlined, involving a corresponding increase in costs in order to maintain

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the current efficiency. The circulation must be pushed, and this is followed by increased silver losses in the cathode—a charge which mounts rapidly. 0.1 ounces or 1.5 ounces per ton might be equally good work for different sets of conditions. The increased energy expended in the cell brings the temperature up and helps the tank resistance. As the density increases the relative cost of operating insoluble anode tanks decreases.

In any given case the multiplicity of relations pointed out above must be solved a pair at a time and a set of final heats run off with the winners. We are very much in the same position as when, in hydraulics, we wish to compute the flow over a weir. The velocity of approach enters into the formula, but this presupposes a knowledge of the flow. We use an estimated flow to find this velocity and then solve the equation for the real flow. This figure is used in computing a corrected velocity of approach and so on till the true value of the flow is obtained. In the light of the foregoing it is easy to see why no two refineries use just the same densities and temperatures and so on. A difference in the cost of labor or power or supplies would tip the economic balance to a new reading at once. The situation varies also according to whether or not the refinery is operated by a copper producer. If it is, interest charges on the metals tied up must be reckoned with and the question of output is not so vital, as it cannot exceed the quantity furnished by the smelter. If the plant is a custom one, operated on a toll basis, a period for refining is usually allowed gratis and interest questions, within certain limits, do not arise.

And, finally, when all is said and done, the lowest cost per ton may not be the cheapest cost per ton. This seeming paradox is due to the fact that with a current density somewhat greater than that giving the lowest cost per ton, the output may be sufficiently increased to give greater earnings in spite of the higher cost per unit.

DISCUSSION.

(Communicated before the Meeting.)

DR. W. D. BANCROFT: Mr. Addicks has given us a long list of the factors bearing on the cost of production, for which we are

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truly grateful. I cannot help wondering whether this paper of Mr. Addicks really gives us an accurate statement of things as they are. Mr. Addicks says: "In any given case the multiplicity of relations pointed out above must be solved a pair at a time and a set of final heats run off with the winners." This is certainly not the way to obtain accurate results. The best relative conditions for two factors are not necessarily the best when a third has to be taken into account. Difficult as it is, one must effect a simultaneous solution of the whole problem and not a series of successive solutions of parts of it. This brings us face to face with an interesting dilemma. Either the Raritan Copper Co. has adopted Mr. Addicks's method of determining the best conditions—in which case the results are probably wrong; or it has adopted some other method, in which case Mr. Addicks has not told us how things really are done.

Mr. Addicks vetoes a high current density on account of the excessive circulation and increased silver losses in the cathode. This would seem to be negatived by the results at Great Falls, where the cathode copper contains only one ounce of silver to the ton when the current density is 35 ampères per square foot.

While all the factors mentioned by Mr. Addicks may have to be taken into account, it is also certain that some of them are relatively unimportant. Take the Great Falls and the Anaconda refineries as an illustration. Both are controlled by the same company, and yet one runs at 35 ampères per square foot and the other at about 11. The Anaconda anodes are said to contain more silver than the Great Falls anodes and there is a difference in the cost of power. So far as the outsider can learn, there is no other essential difference in the conditions affecting the two plants. Unless we assume that one of the plants is being operated foolishly, we must conclude that a variation in the silver content of the anode or a variation in the cost of power, or both, is sufficient to warrant a current density in the one case which is more than three times that in the other. No one would learn this from Mr. Addicks's paper and consequently Mr. Addicks has not given us an adequate discussion of the economic balance in electrolytic copper refining.

Mr. L. Addicks: In the first place, Dr. Bancroft takes exception to my allusion to the race-course. Perhaps my language was

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a little more picturesque than lucid. Of course, I do not mean to consider the factors two at a time, without taking into account their relative importance; the final economic balance is a summation of balances; and in order to arrive at the final figures we must consider all the various ratios involved; and the only way to consider this is to study the ratios separately first. Now he says I veto a high-current density. I do not veto a high-current density; I only veto a too high-current density. When you say silver loss is 1 ounce per ton, that means, of course, 50 cents per ton; and that is well worth considering. As to the Great Falls and Anaconda question, in the first place, Dr. Bancroft says that the Anaconda copper contains more silver than the Great Falls. I presume he has inadvertently transposed the two, there being several times the silver in the Great Falls that there is in the Anaconda. Now, as power cost is the only thing essentially different in the two cases, the different current densities naturally follow, and some of the other conditions I brought up do not enter into it, for the simple reason that they are alike in both cases; and I cannot see that the Great Falls and Anaconda illustration is anything but a very good confirmation of the principles I laid down.

MR. CARL HERING: It seems to me that when a problem involves so many variables, the only really satisfactory way of finding the best conditions is to work out a series of problems assuming various different conditions, as though you were going to operate the plant under each of these groups of conditions, and then plot the results and find the minimum or the maximum point from the curve. At the same time, I think a great deal can be learned by comparing only two variables together, because in that way we can find out the effect of varying one of the conditions by itself. This will aid in getting at the final result.

MR. ADDICKS: I would like to say that the final curve that, as Mr. Hering says, we must plot, can only be plotted by first plotting all the individual curves between the different relations; because we cannot take the plant and run it under all these different conditions when we are considering it on paper, and if we have an actual plant to handle we cannot go to extremes with it.

MR. HERING: As an illustration of the method which I spoke of just now, I had occasion some years ago to work out what was

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then popularly termed the "smashing point" of incandescent lamps. Taking into account the cost of the lamp, the cost of power and the gradually reduced efficiency of the lamp, and drawing the curve, a very interesting minimum point is found, at which point you are sure that it pays better to throw away the lamp than to run it any longer. I give that as an illustration of a practical case involving a number of variable factors.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 8, 1904, President Richards in the Chair.

REMARKS ON PROF. JOS. W. RICHARDS' THEORY OF HEAT OF NEUTRALIZATION AS PRESENTED TO THE SOCIETY, SEPTEMBER 19, 1903.

By Gustaf M. Westman.

When a layer of water is poured over a solution of ordinary salt, the salt itself begins to move upward in the solution until the whole mass is uniform. This phenomenon, which is called diffusion, depends on the centrifugal force of the rotary movements of the molecules, which force acts against gravitation.

If, instead of placing water directly over the solution, a certain kind of membrane be first placed between them, the water will rise above the water level[1], producing a hydrostatic pressure called osmotic pressure, which may attain a value of several atmospheres. This membrane must be one which will allow the water to pass through it, but will not allow the solution to pass.

This pressure increases slowly, corresponding to about 1 decimeter per hour. A direct measurement of this osmotic pressure shows that it follows Gay Lussac's law for gases, the pressure being equal to a gas pressure.

Notwithstanding the fact that this osmotic pressure follows the laws of gases, neither the solution nor any part of it can be considered as a gas, and the pressure cannot be established unless this membrane is placed between the water and the solution during a sufficiently long time. The reason for this is that the centrifugal forces cause a lateral pressure having an upward tendency; this pressure on one side of the wall is opposed by an equal pressure from the opposite side. As the solution cannot pass through the membrane, its upward tendency is impressed on the water with a force equal to the whole force that the substance can exert by its rotary movement.

This lateral pressure can, however, cause the boiling point to

[1] In a vertical tube connected with the solution.

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become higher and the freezing point to become lower, because the molecules must expand in both cases, just as with water.

If these facts are applied to the theory of the heat of neutralization, as presented in a paper by Prof. Joseph W. Richards, read before the Society, September 19, 1903, it can be shown whether this theory holds good. In order to explain the heat of neutralization it is assumed by Professor Richards that the dissolved molecules are in a gaseous condition, as is shown in the following quotation from his paper:

"Solution is a process by which the spatial relations of the molecules of the dissolved substance are indefinitely extended, and by which, therefore, the substance takes on the molecular condition of gaseous state. A cubic centimeter of solid NaCl dissolved in 1 cubic meter of water passes as certainly into the gaseous condition as if it had been vaporized, for the molecules of salt are further apart in this dilute solution than they would be in vapor of NaCl."

When snow is formed in moist air the molecules are still farther apart. Why should we on this account have reason to say that these solid molecules are in the gaseous state, especially as the heat capacity of the snow is much nearer to the heat capacity of steam than to that of liquid water. What characterizes the gaseous state is that the ether around the molecule has a fixed volume, and the ether emanates from and remains with the molecules, which are different from those of water in the form of a liquid.

This gaseous state of NaCl, however, is not used by Professor Richards in his calculation of the heat of neutralization, but instead of it, he assumes that 1 molecule of water has gone into the gaseous state, and that 6.15 atmospheres of pressure is exerted by that molecule.

The value of the latent heat and that of this tension agree quite closely with the heat of neutralization, but we cannot consider this to be the cause of it, for the reason that neither H_2 nor O can pass from its liquid into its gaseous state without compensation, and the pressure cannot act before it is developed.

The latent heat, in my opinion, consists of two factors, one of them representing the energy for separating the molecule from the attraction of the other molecules, and the other representing the energy required for surrounding this molecule with ether in

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order that this attraction may be neutralized. If we concede that the mixing of both of the solutions forms a new molecule of H_2O, where does the ether come from which keeps it separated from the other molecule? Certainly not from any of the solutions, and not from the process of mixing them together.

How the steam at that high pressure, namely, 6.15 atmospheres, remains in solution, is not described. It seems to the writer that if this were true it would pass out of the solution with explosive velocity, and before it is condensed; this is all the more true when we consider that the space occupied by the steam would be as great as that of the whole solution, the temperature of which is raised several degrees.

The heat of neutralization is manifested instantly, but condensation is slow at elevated temperatures. The pressure, as stated above, cannot take place without the membrane, and it requires time to develop it.

The osmotic pressure follows the law of Gay Lussac for gases, namely, that the pressure multiplied by the volume and divided by the temperature is a constant, and all direct methods which are used for determining it employ this formula for constant temperature when the difference of temperature does not exceed 1 degree. Neutralization causes a difference in temperature of several degrees; therefore, this formula for osmotic pressure cannot be applied under this circumstance.

For the reason given above the author does not consider Professor Richards' theory of the heat of neutralization, as stated in the above-mentioned paper, to be well founded, and the present author must also object to the statement that ionization is in no sense to be regarded as a re-solution or decomposition of the molecules into the constituents. As in the case of gases, the ether separates and supports the molecules in exercising the centrifugal force, so in the case of solutions the water separates the molecules from each other, in order that their centrifugal force can act, which is not possible when they are bound together.

When more water is added the molecules expand farther and their constituents are farther removed from each other, so that the attraction between them grows less.

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DISCUSSION.

DR. H. S. CARHART: The author proceeds in this paper as if he were basing his conclusions upon certain facts (mark the word "facts," if you please), which he first states. Now it seems to me that what he proposes here as facts are nothing but the most extreme speculations. He speaks of centrifugal force and of rotary movements. Certainly, that can be nothing except pure theoretical speculation; and whatever his conclusions may be relative to the position of Professor Richards, I cannot see that this argument can amount to anything if it purports to proceed, as it does, from a statement of facts; because it proceeds from speculation and not facts.

PRESIDENT RICHARDS: Any further discussion? In concluding the paper, Mr. Westman says, "As in the case of gases the ether separates and supports the molecules in exercising the centrifugal force, so in the case of solutions the water separates the molecules from each other in order that their centrifugal force can act, which is not possible when they are bound together."

I do not understand at all what that sentence means; but taking Mr. Westman's statement for what it is worth, and in connection with his statement that "in solutions the same thing happens as in the case of gases," I think that his conclusion is virtually a confirmation of my own position, viz., that the state of being in solution is a state very closely analogous to the gaseous condition—whatever theories you may have to explain it.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 8, 1904, President Richards in the Chair.

THE ENERGY OF IONS.

By Louis A. Parsons.

In a communicated discussion of a paper of the writer on "Ions and Electrons," appearing in Vol. III of the Transactions of our Society, Mr. C. J. Reed said: "Whatever may be the nature of an electric charge—whether it be an electron, atom of electricity, or etherial stress—an electrically-charged body, atom, ion, or particle of matter is necessarily under tension and always tends to become discharged. In discharging it always gives up energy to an external body through which the discharge takes place. I believe there is no known exception to this statement. The converse is also always true. . . . The discharge of electrically-charged ions or the neutralization of such ions by giving up their charges to electrodes constituting the terminals of any electric conductor or circuit, can occur, therefore, only by the ions simultaneously giving up electrical energy to the circuit. There is an important fact in connection with the theory of electrochemical action, which, judging from its relation to the dominant hypothesis, does not appear to have ever been recognized. This fact is that in no electrochemical reaction does any ion ever give up energy to an electrical circuit or to any other body in the so-called process of discharging or giving up its charges to an electrode and ceasing to be an ion; that is, by becoming an atom or molecule. On the contrary, every atom in passing into an electrolyte and becoming an ion does give up energy to some other body. It seems to me that our conception of electrolytic dissociation should be reversed, and that ions should be considered as devoid of electrical charges, but having a capacity for receiving electric charges—when the ions become charged from an external source—they separate and become atoms."

Again, in Vol. IV of the Transactions (page 178), Mr. Reed says: "My premise in regard to the theory of electrolytic dis-

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sociation is that electrically-charged bodies are always potentially sources of electrical energy. That is, a system composed of two oppositely-charged bodies is always under stress and always tends to discharge itself. . . . When a system of oppositely-charged bodies gives up its charge to an external conductor they necessarily act as a source of electrical energy. If this premise is wrong its fallacy has not been shown. No instance has been cited, no illustration has been found in which the discharge of electrically-charged particles is not, as stated above, a source of electrical energy. Dr. Parsons in his paper says he is not prepared to admit this premise. He does not deny it, however, nor offer a single instance in which it is not true. Is it admitted that a system cannot produce a stress upon itself? Is it admitted that between oppositely-charged particles there is always a condition of stress? If so, my premise is admitted; if not, the term 'electrically-charged' loses its meaning. If there is any member here prepared to refute this premise I shall allow him to interrupt me now for that purpose; if not, I shall proceed on the supposition that this premise is admitted, namely, that oppositely-charged particles necessarily constitute a source of electrical energy." He then states that if ions are charged, a process of changing ions into atoms at the electrodes must evolve energy. "The facts are entirely opposed to this conclusion—I have not yet been able to find any case in which an ion gives up energy to the electrodes or external circuit in becoming an atom."

Since I had not the pleasure of being at the meeting of the Society, I shall now avail myself of the privilege of questioning Mr. Reed's premises and his fundamental conclusion from it. The argument appears to be this. Two oppositely-charged bodies constitute a source of electrical energy. When they are discharged through an intervening medium energy is evolved or work done upon that medium. If, according to the accepted theory, ions are charged, in the formation of atoms from ions the latter must be discharged, thereby adding energy to the circuit. In all known changes from ions to atoms there is an absorption of energy from the circuit and not an addition of energy to it. Therefore ions must be uncharged and atoms charged.

Now in this chain of reasoning there are some obviously very weak links. First, as to the premise. I certainly will not deny

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that if you connect two charged conducting bodies by a conductor of finite resistance that the bodies will be discharged and work will be done upon the connecting medium. But when the premise in this form is admitted the conclusions do not necessarily follow. Must we look at a positive and a negative ion as two oppositely-charged bodies which are connected by a conductor—the external circuit—making contact with them at the electrodes *a* and *b* (Fig. 1)? If so, of course they will discharge through the external circuit adding energy to it. If, then, the ions thus discharged are atoms, the conclusion follows easily. But what justification is there for considering the action to be like this? No one surely has pictured the action in this way or has supposed that the ions are like conductors making contact with the opposite electrodes and mutually discharging themselves through the medium of the electrodes and the external conductor. If they are like charged metallic spheres would not the + and — ions certainly move toward each other and discharge by mutual contact rather than move away from each other and discharge through the external circuit? And if they discharge by mutual contact no energy will be added to the external circuit. Would there be anything to cause such spheres to move up to the electrodes *a* and *b* and be discharged? Yes, by putting a — charge on *a* and a + charge on *b* great enough to overbalance the attraction between the spheres *c* and *d*. Then *c* would move up to *a* and discharge, and *d* would move up to *b* and mutually discharge. This discharge would add no energy to the external circuit, but would take energy from it. In order to maintain the charges on the electrodes *a* and *b*, so as to make possible the continuous motion of charged spheres—or "ions"—toward the electrodes and the "discharge" of the same there must be a continuous supply of energy by the external circuit. Hence the only possible way as far as I can see in which moving-charged spheres can become discharged by the medium of an external conductor is by a process which obviously requires the absorption of energy from the external conductor and not the addition of energy to it. Considering the ions as simple charged conducting spheres (as Mr. Reed apparently

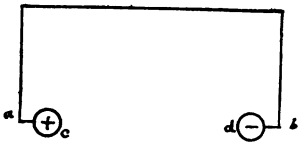

Fig. 1

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does), free to move in a dielectric medium, their discharge in the only way which is possible through the medium of an external conducting circuit is not a source, but a sink of electrical energy as regards the external circuit. If Mr. Reed be right that in saying "in all known changes from ions to atoms there is an absorption of energy from the circuit," then as far as I can see the only legitimate conclusion is that ions are discharged and atoms are not—diametrically opposite to the conclusion which Mr. Reed challenges any one to dispute.

But I do not believe we are justified in considering the ions as spheres or simple bodies with + and — electric charges on them and the atoms as these spheres "discharged" in the sense of having given up their charge to some external body. It does not follow from the ionic theory and is certainly opposed to the electron theory. Hence, even if it were proved, or allowed to be assumed, that charged bodies in discharging always add energy to an external circuit, and if it also be true that ions always absorb energy in changing to atoms, it would not follow that ions are uncharged and atoms charged. We must consider an atom or an ion not as a simple charged body but as a complex electrical system.

Let us first consider the simplest system. Let the ions as before be particles carrying + or — electric charges and let a molecule consist of a + and — ion in union. No discharge of the ions is necessary to form the molecule. In fact it is the charges on the ions that hold them together to form the molecule. All the electric stress is exerted between the two ions inside the molecule, there is no electric field outside, the presence of charges on the ions cannot be detected outside of the molecule, and if we cannot get inside the molecule we will conclude that there are no charges inside, or that the ions have become discharged. In the molecule the ions cease to be ions or "wanderers." They act differently, producing no electrical attraction on outside bodies and are called "atoms." Their charges are still there and they are not devoid of electrical energy, although it is concealed within the molecule.

If the only energy we are concerned with lies outside the molecule, are we not justified in saying that the ions within the molecule are discharged or are virtually without charge? Can we tell whether they are actually charged or not? If we adopt the defini-

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tion of a charged body, or particle, as one which produces an external field, then the molecule is not charged (or we may say the atoms in it are not charged). There is nothing inconsistent or mystical about that. Is there any reason for concluding then that the energy of an "uncharged" molecule must be less than that of the charged ions into which it may be separated? If E^i be the internal energy of the molecule, E_e the external energy of the field, due to the atoms in the molecule E'_i and E'_e the same when the two are separated as ions, and W is the work done in separating them, we have by the conservation of energy,

$$E_i + E_e + W = E'_i + E'_e.$$

That $E_e < E'_e$ is evident, for in the former no field exists, *i. e.*, $E_e = 0$, while E'_e is the whole energy that we can detect. In the case of two simple spheres as ions, $E'_i = 0$, but for more complicated systems we would have no right to assume it. In the case where $E'_i = 0$ we have

$$E'_e - E_i = W.$$

There is no *a priori* reason, as far as I can see, why E_e is necessarily greater than E_i. It is so provided $W > 0$, that is, provided work be expended to separate the ions, or if they tend to change back to molecules. But if the tendency is the opposite way, *i. e.*, if $W < 0$ then $E_i > E'_e$. It may be objected that this latter is impossible for actual charged spheres. True, for simple spheres, at rest remaining in the same dielectric, for it always requires work to separate the two opposite charges and hence they must possess the greater energy when separated, or better stated, the medium possesses more energy when they are separated. But this is necessarily true only of such bodies whose only energy lies in the stress of the medium between. In the case of ions, not only are other forms of internal energy not excluded, but they are necessary consequences of every one of the theories which have had wide acceptance, such as different theories of ions, the electron theory and the vortex theory. And, as I have attempted to show, and will farther attempt to show, this is not at all antagonistic to known laws of electric force and energy.

But let us first pursue the consideration of the ions as simple

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charged bodies. The two oppositely-charged ions are held together in the molecule by the electrostatic force of attraction between them. If the electric charges be + e and — e the distance apart, r, and the dielectric constant of the medium is K, this force of attraction $= \frac{e^2}{Kr^2}$ (r is an intermolecular distance). At distances of a higher order than the dimensions of the molecule no force is exerted, no stress exists, and hence the molecule is "uncharged." Suppose, also, that the parts of the molecule possess kinetic energy which would send them apart if it were not for this force of attraction. Let F = the force tending to separate them. Evidently since they are held together

$$\frac{e^2}{Kr^2} > F \text{ or } \frac{e^2}{Kr^2} = aF$$

where $a > 1$

Let the molecule now be put into another dielectric of specific inductive capacity K′. No energy is added save the work done in putting the molecule into the new dielectric. The force now is $\frac{e^2}{K'r^2}$. If K′ > K the force of attraction is decreased and the electric potential energy is decreased. If K′ $> a$K the force

$$\frac{e^2}{K'r^2} < F$$

and the parts of the molecule move apart, *i. e.*, they become "wanderers," or ions. As they move apart the lines of force that formerly bound them together move outward and extend through the dielectric, *i. e.*, they become charged. Clearly, then, their energy when charged is less than when uncharged. This, then, is thoroughly in harmony with the idea that the ions are charged and the molecules not, and also that the ions have the less energy.

Placing a substance in a dielectric which can penetrate between the parts of the molecule will, if the specific inductive capacity be great enough, cause a separation of the parts into charged constituents of the molecules—*i. e.*, a dissociation into ions. J. J. Thomson has shown, however, that it is not necessary for the dielectric to actually penetrate between the parts of the molecule

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in order to cause a lessening of the force and a separation of the parts. It does not follow from this that if any are dissociated all must be, or that the dissociation of any given set of ions is permanent. The parts of a molecule may separate and drift away as charged ions; a positive and a negative ion may then be drawn together by their mutual attraction and unite for a time, but the union is not stable and the equilibrium may at any instant be overthrown and dissociation occur again. An explanation of increasing dissociation with increasing dilution, or a statement of a law governing the number of molecules dissociated at any one time is not essential to the argument here. In the case of the solution of a salt in water there occurs, according to the dissociation theory, a separation of the molecules, or a part of them, into charged ions. Now water is known to have a high dielectric constant—about 76. Hence, if we can consider the water as entering within the molecule the change in the dielectric constant will be enough to easily explain the dissociation and the consequent action. It cannot be said that this is impossible—the assumption violates no essential law. Where does the energy come from which causes the dissociation? I answer, no energy is necessary unless work is required to force the new dielectric between the constituent parts of the molecule. And is it not most natural to assume that it is during the process of solution that the dielectric is brought to this position. Solution itself we know in many cases absorbs heat energy from the solvent. If this is the energy which in the process of solution brings about the relation of the dielectric and molecules of the solute, it by no means follows that the solvent must furnish a constant source of energy as recombination and ionization continually progress, or as ionization proceeds when ions are by any means removed from solution. The work has been done in bringing about the relation of molecules and dielectric, as a result all the molecules may be in an unstable state, some separate as ions, others ions unite, the unstable equilibrium being controlled by the number of free ions at any time. If, then, any of these are removed others consequently would be dissociated without the expenditure of any energy. As to the removal of the ions, that, however, may require external energy, but it need not come from the solvent.

As long as there is nothing but the solvent and dissolved sub-

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stance present dissociation and recombination progress side by side and equilibrium is maintained. No electrical energy is evolved or absorbed. Now put into the solution two pieces of metal, A and B (Fig. 2), having a metallic connection C above. In the solution are + ions and — ions. Is there any reason for imagining that all of the + ions will move, say to A, and all the — ions to B, that they will make contact and mutually discharge through the medium of the connection AC, B? From all we know of charged particles they certainly would not do that. But if they did, they would not pass out of solution. The "discharged" ions would not be molecules and, discharged in this way, they would not be atoms, and would be totally incapable of uniting to form molecules. Then what would happen? A little ionization of the metal at both A and B, an interchange of ions, a little chemical action, but certainly no electric current along C, no electrical energy added or subtracted. Let, however, a + charge be placed on A and a — charge on B. An electrostatic field is now produced in the solvent. + ions immediately move toward B, and — ions toward A. What happens when the — ions reach A? Do they all discharge? If so, the + charge on A is used up and similarly the — charge on B, and in order to maintain the potentials of A and B, and cause the continual motion of the ions and their discharge, an e. m. f. must be inserted in C and electrical energy added to the circuit. But as has just been said the discharged ions cannot form molecules. Suppose, however, two — ions move up to A. The first to arrive gives up its charge to A (or an ion from A), neutralizing some of the + charge from A and taking energy from the circuit, and then receives a + charge from A (taking more energy from the circuit). Having now a charge similar to that of A it is repelled back from it and meets ion No. 2, which has a — charge. The two being oppositely charged unite, forming a molecule. If it is a molecule of gas or an insoluble solid it is freed from the presence of the solvent as a dielectric, the electric force inside the molecule is hence much greater than in the case of a molecule in solution, hence the molecule which separates from the solution is stable. After the molecule is formed, it may

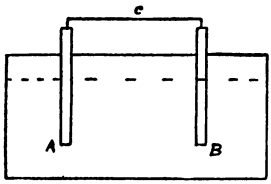

Fig. 2

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chemically react with molecules in the solution or with molecules of the electrode A, or when the — ion comes up to A it may unite with a + ion from the metal A, forming a molecule of a compound. This + charge is then taken away from it. In either case we have a result which agrees in all respects with the actual result, and that upon the supposition that the ions are charged, which premise in all cases leads us to the conclusion that energy must be supplied to the circuit to cause this change of ions into molecules agreeing with the facts as we know them.

If A and B are not of the same metal the local effects without any e. m. f. in C. — ionization and chemical action are different at A and B, AcB is a metallic circuit and tends to maintain the same potential throughout. The molecules of both A and B tend to ionize and pass into solution but one more than the other. Let + S (Fig. 3) be the + ion, — S′ the — ion of the dissolved substance, + A, a + ion of the metal of the electrode A, etc. Consider a molecule on the surface of the electrode A, $\overset{+}{A}\overset{-}{A}$. The solvent is in contact with it, the ions + S and — S′ come up to it. The presence of the dielectric (the solvent) may disturb the equilibrium of the molecule AA and the attraction between + S and the — part of AA, or between — S′ and the + part of AA, may become greater than the force holding AA together and cause the ionization of AA and the union of one of these ions to one of S′. As to which combination will take place depends upon the chemical nature of the molecules—the stability of the intermolecular attractions. Suppose that + A unites with — S′ (the case of a zinc electrode dipping in sulphuric acid). A continuation of this action leaves an excess of + S ions in solution and an excess of — A ions in contact with the electrode. The — A ions being in contact with the electrode may hand over their charge to the electrode, lowering the potential. The potential of B is consequently lowered also (a current flowing from B to A). This is equivalent to putting a — charge on B, which will attract toward it the + S ions in solution. But if B acts in the same way as A, a similar action in the opposite direc-

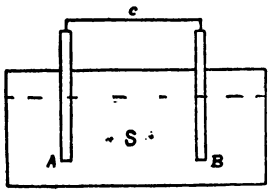

Fig. 3

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tion will occur. If the action at A is greater than at B a current will flow through the solution from A to B and through the wire C from B to A, preventing the union of + B and — S′ causing a motion of — S′ toward A and of + S toward B. This is the action of a primary cell. Now as to the most important question, whence comes the energy maintaining the current in C? Instead of using up energy from its external circuit energy is given to the external circuit. We start with molecules AA and ions + S and — S′ and end with ions — A (at the electrode) and + A and — S′ (in solution) and SS molecules. Since energy has been given to the circuit we must have.

$$\text{Energy of } AA + \overset{+}{S} + \overset{-}{S'} < \overset{-}{A} + \overset{+}{A} + \overset{-}{S'} + SS$$

This involves the supposition that the energy of the molecules AA is greater than the ions A A, which has already been shown to be in harmony with the idea that the ions are charged.

Thus, the case of ordinary electrolytic action (where electric energy is supplied by an external circuit) and of the primary cell (where energy is furnished to the external circuit) are both explained readily upon the supposition that the ions are charged, which explanation is based simply upon our known laws of the actions of electrically-charged bodies and violates neither the conservation of energy nor any other great principle.

These explanations have been based upon the simplest consideration of the constitution of the molecules and ions or atoms. There is, however, a great deal of evidence that the atom, ion and molecule are much more complex, the atom being a rather complicated system in itself, containing electrons or "atoms of electricity" revolving in orbits of their own. These electrons possess electro-kinetic and electro-potential energy. The energy of ions and molecules may then consist of several different forms besides the energy of the external field due to charged ions. Unless we know all about the energy in the two cases we cannot arbitrarily say that the energy of "charged" ions must be greater than "uncharged" molecules or even atoms. We could never be justified in such an assertion until we had shown the sum total of all the energy in a molecule or uncharged atom must necessarily be less than the energies of the charged ion. We must

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take into account the electro-potential and electro-kinetic energies of the electrons, the mutual energies of the different electrons, the mutual energies of the electrons and atoms, and the mutual energy of the atoms in the molecule besides the energy of the external field.

You may show me two base-balls, one lying on the ground and one flying from the bat, and tell me that the latter has more kinetic energy than the former, and I will believe you. But when you say having admitted this, I must also admit that the energy of a keg rolling down hill is greater than that of another keg (weighing the same, if you please) standing still, I will reply, "No, indeed, not yet; let me first take the head off of this keg, perhaps I will find a large gyroscope within running with great velocity." When I am told that connecting by a wire two balls oppositely-electrically charged and thus causing them to discharge reduces their electric energy, I as readily agree, as in the case of the base-balls, but when I am told "therefore" if ions are charged, their change to molecules (or atoms) must evolve energy, I by no means assent. I confess that my mind is so constituted that I cannot admit the validity of an argument from this kind of analogy—reasoning from the simple to the complex.

The ionic theory for solution, or the electrolytic dissociation theory, as it is called, has proved very fruitful and is certainly deserving of our respect. I am far from maintaining that it is perfect or incapable of improvement. Nor do I contend that facts may not be brought to light that may eventually entirely overthrow the theory, and, if so, we ought in the true scientific spirit be prepared to cast it aside. But I think that is hardly likely. That modification will be necessary is very probable. I am inclined to think that modification will be brought about in line with developments in the broader theory of electrons. But will it lead us to the final true solution to cast the whole theory overboard, after it has in many respects been so successfully tested, has inspired so many valuable researches, and led to important discussions, and has been the cause of so much careful study directed both in its defence and in opposition to it—and having cast it aside to put nothing in its place or else put in a new and untried theory out of harmony with other related theories which seem well substantiated, and which appear to be no better an

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explanation of the main facts as we know them? That the dissociation theory—or the ionic theory for solution—has its points of weakness, I will not attempt to dispute. But what I contend is, since it has proved a very useful theory, has explained many facts, has been decidedly fruitful, and since no better theory has been offered as a substitute it should be allowed to stand until something obviously better is offered in its place. If it has not been proved to be true, certainly it has not been shown to be impossible. It does not necessarily violate either the conservation of energy or any other established principle of physics.

University of Utah,
Salt Lake City, Utah.

DISCUSSION.

MR. C. J. REED: I have read this paper over and I failed to find anything that seemed to require any extended answer. Dr. Parsons has put forth a theory of his own, instead of the theory of electrolytic dissociation, and it is a theory that I did not attack in my paper. One of his admissions (and which, I think, decides the whole matter, so far as his argument is concerned), is that if we take a molecule out of one medium into another having a greater specific inductive capacity, the constituents of the molecule, if they are oppositely charged, will separate; but he forgot to state that in that case it would always require energy to change the molecule from the one medium to the other, consequently it would always absorb energy to dissolve a salt into a solution in which it became ionized. Take the case of zinc chloride, for instance, or any salt which on going into solution evolves a large quantity of energy: how can that be accounted for on any such supposition? We must admit that in that case a compound is being transferred from one medium to another of higher specific inductive capacity, and consequently that operation must require energy. Where does it come from? As a matter of fact that operation gives out energy. I am as yet unable to see, and I have not

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found anyone who has been able to describe, the process by which any substance in a chemical reaction can simultaneously absorb and evolve energy. We cannot claim that both the heat evolved in solution and the energy required to separate the ions come from the intrinsic energy of the zinc chloride or the water, because only that which appears as heat is accounted for in the complete cycle of changes in which zinc passes from the metallic state into the chloride, thence into ions, and finally again into metallic zinc.

MR. H. L. CABOT: It is a subject about which I know very little, but it strikes me that Mr. Reed's last contention does not fully cover the case. What we perceive when zinc chloride or sulphuric acid or any other substance that emits heat on addition of water, is dissolved in the water, is not every item of change which takes place, but it is the net result. There is nothing inconceivable in the supposition that zinc chloride in being converted from a solid to a solution thereby requires a certain amount of energy which—if that were the whole story—would be attended with a corresponding evolution of cold or absorption of heat; but if zinc chloride has an affinity for water, naturally in being dissolved in the water, the taking up of water would be attended with heat which evidently is greater than the amount needed for the change in its actual physical condition, and I do not see—it is a familiar theory of chemists that all breaking up of bonds is attended with absorption of heat, and yet we know a great many apparent exceptions to that, such as the explosion of gunpowder and the explosion of nitroglycerine, where there is an immense evolution of heat, but that evolution of heat is not due to the breaking up, but due to the subsequent combination.

DR. E. F. ROEBER: Mr. Reed says that the paper represents Dr. Parsons' theory, not the dissociation theory, and then Mr. Reed takes exception to Dr. Parsons' remarks on the relation between the dielectric constant and the ionizing power of a solvent. In this Dr. Parsons seems to follow the views of Thomson and Nernst, and the Nernst-Thomson rule is a more or less accepted part of the dissociation theory. Two bodies charged with given quantities of electricity exert on each other a different attracting or repulsing force in air than, for instance, in petroleum. This is an experimental fact. The high dielectric constant of water necessitates that the attraction between the charged particles of a mole-

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cule is small. Concerning the application of the energy question to this point, I agree with Dr. Parsons.

MR. REED: From a series of reactions which will form a complete cycle you must take into account all of the changes in that cycle, and that is not what is taken into account in the theory of electrolytic dissociation. If we start with zinc and chlorine, these two substances unite and give out energy. If we add the zinc chloride formed to water, these two again unite and give out energy. Now, according to the theory of electrolytic dissociation they are now in the dissociated state, the zinc and the chlorine are in the condition of oppositely-charged particles—oppositely-charged spheres. If in that condition we have oppositely electrically-charged spheres which give up their charges by becoming neutralized, that is a process which must necessarily give out electrical energy to the circuit through which they become neutralized, whether that circuit is an external wire or whether it is the material of the particles themselves. That is a point which Dr. Parsons disputed, but he did not, in my opinion, give any reasons. It seems to me that if we have two oppositely-charged particles, it makes no difference whether we connect them with a wire of different material or whether we connect them by bringing together the material of the particles themselves. In fact, when two oppositely-charged particles are connected by wires, the wires may be considered as merely prolongations of the particle itself, and if those wires are brought together and form a circuit, we may consider them as merely prolongations of the spheres. When opposite electrical charges are neutralized in that way by coming together and discharging, I think there is no exception to the fact that electrical energy must necessarily be developed in the body through which that discharge takes place, whether it is the body of the spheres themselves or projections upon the spheres which we might call wires. That process must develop electrical energy. If in that process these ions become atoms of zinc and chlorine, then we have three consecutive processes starting with atoms and ending with atoms, a complete cycle of processes, each one of which gives up energy, that is, the atoms give up energy in each case to something else. First, the atoms of chlorine and zinc give up energy in uniting in the form of heat; secondly, they give up energy again in uniting with the water;

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and, thirdly, if they are charged particles and become discharged, they must give up energy in changing back again into the condition of chlorine and zinc atoms—what we originally started with. Now it seems to me that it is a waste of time to talk about absorbing and simultaneously evolving heat in a certain part of that circle; we must take the complete cycle of those operations, and we cannot find in any portion of that cycle a place where energy is absorbed, except in changing from ions to atoms, from charged to discharged bodies. And this is exactly what should not be found if the ions are charged and the atoms discharged.

DR. ROEBER: A chain is no stronger than its weakest link, and the weak point in Mr. Reed's cyclic process is its third step. This third step is based on the assumption that the change from an ion to an atom always evolves energy. This is the point which has been discussed at length at our last meeting in Niagara, and in Dr. Parsons' paper. No advocate of the electric dissociation theory will agree with Mr. Reed on this point.

PRESIDENT RICHARDS: I wish on my own part to call attention to something that is not clear to me in Mr. Parsons' paper (page 136), wherein, at the top of the page, he says, "The two oppositely-charged ions are held together in the molecule by the electrostatic force of attraction between them." When I first learned chemistry, I learned that an electropositive element tended to unite with an electronegative element to form a chemical compound. I do not see any difference between Mr. Parsons' statement and the ordinary definition of a chemical compound, if we read atom for ion. Two oppositely-charged atoms are held together in a molecule by the force of attraction between them. It seems to me that if "chemical combination" means anything, Mr. Parsons' statement means that the two ions are combined as a chemical compound.

MR. REED: And not dissociated.

PRESIDENT RICHARDS: They are combined, whatever you call combination—in a combined condition. Further down, Mr. Parsons says, "and the parts of the molecule move apart, *i. e.*, they become 'wanderers,' or ions." That is, he starts with them as two oppositely-charged "ions" held together by electrostatic force, and then he says that they *subsequently become ions*. I confess I cannot understand that.

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DR. ROEBER: There seems to me no difficulty in this conception. This is essentially the view of the Nernst-Thomson rule. A molecule of NaCl consists of an atom Na with a positive electron and an atom of Cl with a negative electron. In the ordinary condition they are held firmly together and the opposite electrons do not produce an external field; the molecule appears to be electrically neutral. There are two kinds of forces, one tending to drive the two particles from each other, the other being the electrostatic attraction due to the electrons. Under ordinary conditions the latter prevails. But if we bring the molecule into a medium of high dielectric constant, like water, then, according to the elementary principles of electrostatics, the electrostatic attraction becomes smaller, and the Na atom with its positive electron and the Cl atom with its negative electron tend to separate. This is ionization.

MR. REED: Where does the energy come from?

DR. ROEBER: Parsons speaks about it at length. I don't want to repeat all the paper.

DR. R. GAHL: It might be more instructive to regard this matter from a more chemical point of view, by attributing the electrical charges of both anion and kathion to the combination with electrons. We have to assume that zinc chloride is not only a compound of zinc and chlorine, but contains also positive and negative electrons. If we dissolve it in water, it will dissociate in the same way as other chemicals do following the equation:

$$Zn\,Cl_2 +_2 -_2 = Zn +_2 + 2\,Cl -$$

There is nothing different from other chemical dissociations, if electrolytic dissociation is regarded this way. The laws of chemical mass action may be applied as well, and with regard to the question raised by Mr. Reed, where the energy comes from, it must be answered, that it comes from the same source as every other kind of chemical dissociation.

MR. REED: Are we to understand that electrolytic dissociation does not mean chemical separation?

DR. GAHL: Oh, yes, certainly.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904, President Richards in the Chair.

THE ALUMINUM ELECTROLYTIC CONDENSER.

By C. I. Zimmerman.

INTRODUCTION.—ASYMMETRICAL CELLS.

The property of asymmetrical conductivity, which is possessed by many electrolytic cells, may in some instances be developed to a remarkable degree. An illustration of such cells is one with aluminum and carbon electrodes in an aqueous solution of ammonium phosphate. This cell will allow a current to pass freely when the *carbon* is the positive terminal and will prevent the passage of a current when the *aluminum* is the positive terminal. As is well known, cells of this type (and also cells having fused salts for electrolytes) are the basis of apparatus recently placed upon the market for converting alternating currents into direct currents.

The Film.—The asymmetrical effect of the aluminum cell is located in the thin film which is formed upon the surface of the aluminum electrode by electrochemical oxidation. This film under ordinary circumstances firmly adheres to the surface of the metal, no matter in which direction the current flows through the cell. Its composition cannot be definitely determined since sufficient quantities cannot be collected to be given an accurate analysis. It is believed to be some form of oxide, or perhaps, hydroxide of aluminum.

The factors affecting the formation of a film cannot be here taken up in detail. Suffice it to state, that with fixed operating conditions, the film does not continue to grow thicker after a certain limit has been reached because it protects the metal beneath from further oxidation. The principal factors affecting the growth of a film are the kind of electrolyte, the value of the impressed pressure, the duration of the process of formation and the temperature of the electrolyte. Either alternating or direct currents may be used for the formation, since reduction of the film

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does not occur to an appreciable extent when current flows toward the aluminum plate.

When first formed, the film itself is ordinarily transparent and colorless. Its presence is best detected upon smooth plates by the interference colors which are produced in light reflected from the surface. The presence of these interference colors was noted by some of the earliest investigators of the "polarization phenomena of aluminum electrodes."*

After a short usage the electrode becomes grayish, but the bright colors are not necessarily destroyed. The grayish appearance is due to a slight roughness of the metallic surface beneath the film, and to the presence of numerous minute punctures in the film.

The colors to be observed as a film increases in thickness from zero are greenish-yellow, yellow, orange, red, violet, indigo, blue, green, yellow, orange, etc. The appearance of the greenish-yellow color first means that the light observed by the eye is white light minus some color which will produce greenish yellow light. The light missing is violet light, which is the light with the shortest wave-lengths. The light *blotted out* by interference follows the order violet, indigo, blue, green, yellow, orange, red, etc., as would be expected from the fact that violet light consists of the shortest waves, and red light of the longest waves.

By means of these interference color phenomena the writer has estimated the thickness of the films. They range from less than 0.000,005 centimeters to, in exceptional cases, more than 0.000,050 centimeters in thickness.†

The Condenser.—This extremely thin asymmetrical layer exists between two electrical conductors and it constitutes an asymmetrical dielectric which may be considered capable of holding

* *E. g.*, W. Beetz, Journal der Physik, Vol. 156, p. 456, (1875). (Poggendorff's Annalen, Vol. 244.)

† From a consideration of the interference phenomena produced by a transparent film upon the reflecting surface of a medium more dense than the film, the formula indicating the film thickness is $d = \frac{n\lambda}{4\beta}$; where "d" is the film thickness in centimeters; "n" is an odd number which is 1 for the first range of the spectrum observed, 3 for the second range, 5 for the third range, etc; "λ" is the wave-length in air, expressed in centimeters, of the color of light *observed to be absent in vertically reflected light*; and β is the value of the index of refraction of the film substance which is assumed in this case to be between 1.4 and 1.5, the value corresponding to the indices of refraction of other substances similar in nature to the film.

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positive charges only on the side in contact with the metal, and negative charges only upon the side in contact with the liquid. The disruptive strength of this film when the metal is positive to the electrolyte is apparently greater than that of mica. Its specific inductive capacity is not unity, as has been assumed by some,* if we calculate it from the electrostatic capacity of a given electrode and the thickness of the film as estimated by the color phenomena. On the other hand, the specific inductive capacity seems to be abnormally high for a solid. Mr. W. R. Mott,† in investigating the aluminum anode properties, calculated the dielectric constant of the film to be in the neighborhood of 80.‡

THE ALTERNATING CURRENT CONDENSER.

An electrolytic cell having both electrodes of these coated aluminum plates will obviously prevent a direct current from flowing continuously through the cell in either direction. An alternating pressure, on the other hand, causes a comparatively large current to flow; the current being a leading or condenser current.

A cell of this type (see Fig. 1) constitutes the simplest form

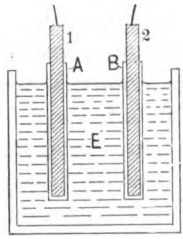

Fig. 1.- ALUMINUM CONDENSER

of an aluminum electrolytic condenser for alternating current circuits. The properties of this condenser do not appear, if we are to judge from the literature of the subject, to have been studied very thoroughly, although the presence of a condenser action has been known as long as the asymmetrical properties of the anode.

It must be borne in mind that these asymmetrical properties are properties of the chain metal-film-electrolyte, and are frequently ascribed to the film or to the electrode for convenience only. When

* *e.g.*, A. Nodon. Comptes Rendus. Vol. 136, p. 445-446, (1903).

† Thesis, University of Wisconsin, (1903).

‡ See communicated discussion by Mott, p. 164, these transactions, for corrected value. —ED.

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dry, the film acts like any ordinary dielectric. Again, when the aluminum electrode is immersed in the electrolyte, it is *not* a perfect asymmetrical conductor or dielectric. In the discussion to follow, perfect asymmetry, no polarization pressures, and no cell losses are assumed to exist. These conditions are only approximated, as will be shown.

In Fig. 1, 1 and 2 represent two similar cell electrodes of metallic aluminum, coated by the thin films A and B, and immersed in the electrolyte E. The electrolyte E is one which is capable of maintaining the continuity of the film by electrochemical oxidation. The films, A and B, are the two dielectrics which, it must be remembered, will allow the current to flow from the electrolyte to the electrodes, but not in the reverse direction, and which can hold positive charges only next to the metallic conductors, and negative charges only next to the electrolytic conductor.

The behavior of the cell upon an alternating current circuit is as follows, with the previous assumptions in mind:

If the cell be connected into the circuit when the alternating pressure is passing through zero and when electrode 1 is becoming positive to electrode 2, a current will flow through the entire circuit in the direction from electrode 1 toward electrode 2. Film A receives an electrostatic charge whose potential rises to that of the pressure upon the cell terminals, for film B allows the free passage of current out of the cell.

When the impressed pressure ceases to increase, the current in the circuit stops flowing. As the impressed pressure begins to decrease, film A tends to discharge itself into the circuit. Electrode 2 now becomes the anode and film B receives an electrostatic charge, positive on the side next to the metal and negative on the side in contact with the electrolyte.

Whatever may be the subsequent variation of pressure upon the cell terminals, the coulomb charge removed from either one of the films must collect upon the other; and *we have* consequently *a condenser in which the total charge in coulombs remains constant.* This statement assumes that the subsequent pressures upon the cell terminals do not rise higher than the maximum value of the pressure which caused the charge to collect in the cell.

This constant charge may be observed in the aluminum cell by disconnecting the cell from the alternating pressure circuit, short-

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circuiting the electrodes, and then connecting a voltmeter to the short-circuiting wire and to a carbon rod dipped into the electrolyte. A discharge always occurs through the voltmeter from the metallic connections to the electrolyte. The short circuiting of the cell is equivalent to removing the cell from the circuit when the alternating pressure passes through zero. Under similar circumstances, an ordinary condenser is completely discharged.

The condenser action of the cell will be shown later to be due to the *distribution* of the charge within the cell. The short circuiting of the electrodes of an aluminum condenser allows an equal distribution of the charges upon the two plates to occur.

A given coulomb charge, q, removed from one of the films as A, lowers the potential difference across the two sides of that film by a definite amount as e. This same charge in becoming stored up in the other film raises its potential by the same amount e, if the two films have equal electrostatic capacities. The *arithmetical* sum of the pressure across the two films is thus constant. The value of this sum is equal to the maximum value of the pressure applied to the cell terminals.

These two film pressures are in opposition to one another. The *algebraic* sum of their *instantaneous* values is equal to the *instantaneous* value of the impressed pressure.

This constant electrostatic charge remaining in the cell at all times sets up a difference of potential between the inside of the cell, or the electrolyte, and a point outside of the cell (in the metallic connections) which is neutral to the alternating pressure. The middle point of an inductance coil placed across the cell terminals represents such a point. In Fig. 2, an alternator G is shown con-

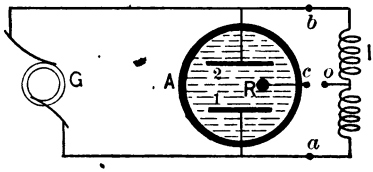

Fig. 2.- CELL PRESSURES

nected across the cell terminals of an aluminum condenser A. An inductance coil I is placed across the cell terminals. By means of a carbon rod R dipped into the electrolyte, the potential of the elec-

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trolyte may be obtained. The polarization pressure that is set up at surface of this carbon terminal will be assumed for the present to be zero, as it is small compared with the generator pressure.

The pressure between the middle point *o* of the inductance coil, and the electrolyte *c*, is a uniform direct pressure as was explained above. The pressure across one-half the inductance coil is one-half the alternating pressure. The pressure between the electrolyte *c* and either of the cell terminals, *a* or *b*, is the *resultant of a uniform pressure* of a magnitude equal to one-half the maximum instantaneous value of the pressure wave impressed upon the cell, *and an alternating pressure*, of a magnitude equal to one-half the effective value of the pressure impressed upon the cell. With an effective sinusoidal alternating pressure E, this resultant is theoretically equal to $\sqrt{\frac{3}{2}} \times E$ or .866 E.*

The average value of the pulsating pressure wave is dependent only upon the maximum instantaneous value of the impressed pressure wave. The average value for a sinusoidal impressed pressure wave is $\frac{E}{\sqrt{2}}$ or .707 E. These pulsating uni-directional pressures upon each film are continuous sinusoidal waves with an amplitude of one-half the alternating wave across the cell terminals, a maximum value equal to the maximum of the alternating wave and a minimum value which is zero.

The average and the effective values of these waves may be measured by means of direct and alternating current voltmeters respectively. The results obtained by such measurements are lower than the theoretical values, due, as was previously mentioned, to the film not being a perfectly asymmetrical conductor, to polarization pressures existing at the aluminum and carbon electrodes and to the small energy losses in the cell. With 100 effective alternating volts applied to the aluminum terminals the readings obtained by alternating and direct current voltmeters are about 77 and 60.5 respectively, the theoretical values being 86.6 and 70.7.

Figures 3 and 4 show these theoretical pressures by means of curves. The three curves, *b-b*, *c-c* and *o-o* represent the potentials of the three points, *b*, *c* and *o* of Fig. 2 referred to the potential of

$$* \sqrt{(\text{eff. DC})^2 + (\text{eff. AC})^2} = \sqrt{\left(\frac{E}{\sqrt{2}}\right)^2 + \left(\frac{E}{2}\right)^2} = \frac{E\sqrt{3}}{2}$$

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one of the cell terminals *a*. Curve *d-d* will be referred to later. Horizontal distances indicate time from any assumed instant as M-M.

The instantaneous differences of potential between the middle point of an inductance coil, the electrolyte and the electrodes are represented by the vertical distances between the curves marked correspondingly. The impressed pressure is represented by *b-b*,

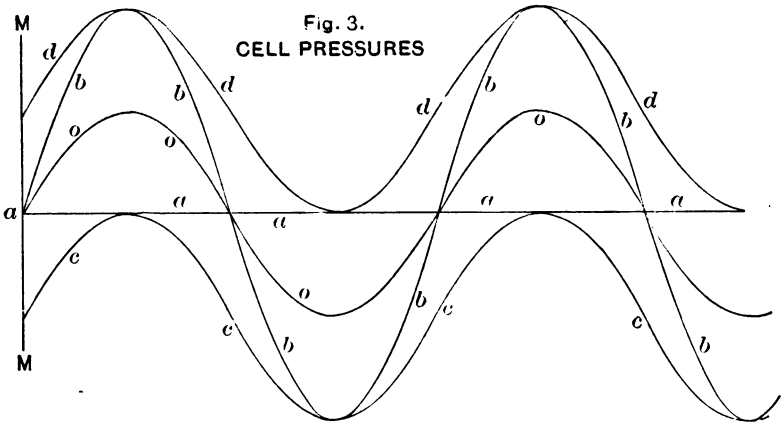

Fig. 3.
CELL PRESSURES

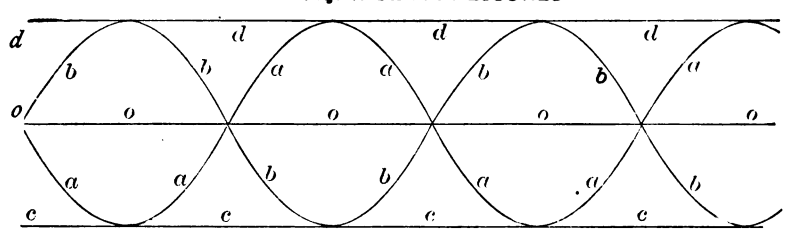

Fig. 4. CELL PRESSURES

measured from the horizontal line *a-a*. The vertical distances from *a-a* to *o-o* represent the potential differences between the terminal *a* and the terminal *o*, or one-half the impressed pressure. The vertical distance between *o-o* and *c-c* represents the constant potential difference existing between the middle, *o*, of the induction coil and the electrolyte, *c*, the electrolyte remaining negative at all times to the middle point, *o*. The pressure between the cell terminal, *a*, and the electrolyte, *c*, is similarly seen to be repre-

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sented by the vertical distance between *a-a* and *c-c*. This pressure is a pulsating unidirectional pressure whose pulsations are continuous sinusoidal waves. There is one pulsation for each cycle.

Between the electrolyte and the other electrode there is a similar pulsating pressure which, in Fig. 3, is represented by the vertical distances between *c-c* and *b-b*. The ordnates to the curve *d-d* from *a-a* represent this last pressure if one of the lines as *c-c* be considered for the moment a straight line coinciding with *a-a*.

Fig. 4 represents these same cell pressures referred to the potential of the middle point of the inductance coil, instead of one of the electrodes.

The pulsating pressures upon the films are shown in Figs. 5 and 6 in curves taken from oscillograph records. The impressed pressures were similar in shape to these waves. Their amplitudes were

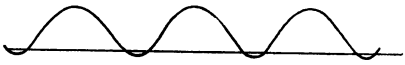

Fig. 5. PRESSURE ON FILM
(OSCILLOGRAPH CURVE)

Fig. 6. PRESSURE ON FILM
(OSCILLOGRAPH CURVE)

twice as great and they were symmetrically disposed with respect to the straight line. The curves are observed to cross the zero line slightly, due to imperfect asymmetry, polarization pressures, cell losses and to the effect of the oscillograph in removing a portion of the charge in the cell.

In Fig. 7 are shown oscillograph curves of all the cell pressures and also the charging current of a 40 microfarad condenser, superimposed upon one another. The impressed pressure was 100 volts and of a triangular shape. Curve *b-b* is the impressed pressure referred to *a-a; c-c* is the pressure between one of the cell terminals and the electrolyte referred to *a-a;* and *d-d* is the pressure between the other cell terminal and the electrolyte as seen by the

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oscillograph. These curves correspond to curves *b-b, c-c* and *d-d* of Fig. 3 respectively. The charging current of the condenser, *i-i,* is flat-topped because the pressure wave is triangular in shape.

An electrical analogy of pressures combined to produce these

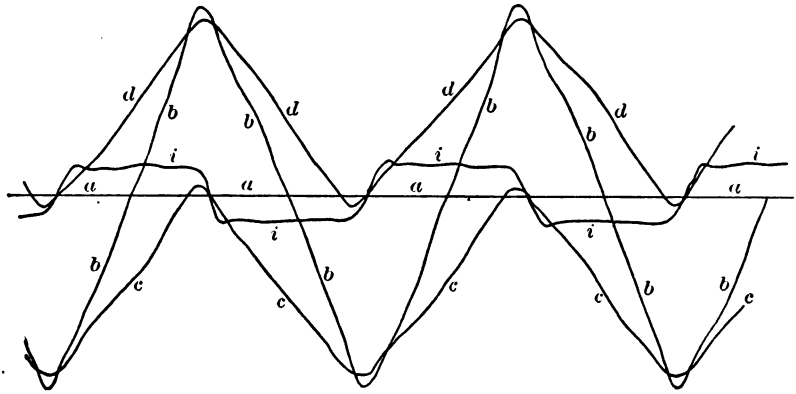

Fig. 7. OSCILLOGRAPH CURVES

same results is shown in Fig 8. G_1 is an alternator giving a sinusoidal pressure E_1; G_2 is a constant pressure machine whose positive brush is connected to the middle point of an inductance coil I. If the constant pressure have a value of one-half the *maximum*

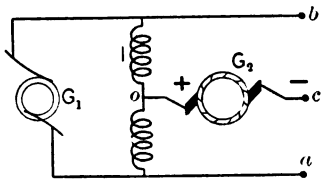

Fig. 8

value of the alternating pressure E_1 (*i. e.* $\frac{E_1}{2}$) then the same pressures will be produced between the free terminal *c* of the constant pressure machine and the alternating terminals *a* and *b* as would exist in a condenser with two perfectly asymmetrical electrodes connected as shown in Fig. 2.

It is not necessary that the two asymmetrical electrodes of an aluminum condenser be placed in the same cell. If (as is shown in

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Fig. 9 by the two cells to the left) two asymmetrical *cells,* each with one aluminum and one carbon electrode be connected together by their *carbon* terminals, and connected to the alternating pressure leads at their *aluminum* terminals, the simple condenser is altered only by the introduction of small polarization pressures within the cells and by additional cell resistance. The pressures between the carbon junction, *c,* and the aluminum electrodes, *a* and *b,* are then practically the same as in the simple condenser.

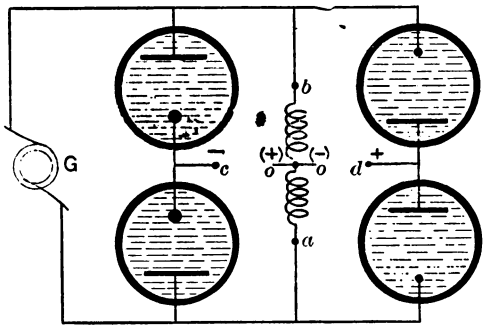

Fig. 9

If in two cells, the carbon electrodes be connected to the alternator leads and the aluminum electrodes be connected together (as shown in Fig. 9 by the right hand pair of cells), the aluminum junction *d* will assume a constant *positive* potential with respect to a point, *o,* neutral to the alternating pressure. The potential difference between the wire, *c,* joining the two carbon electrodes of one condenser and the wire *d* joining the two aluminum electrodes of the other condenser will be twice as much as the pressure between either of these points and the neutral point of an inductance coil.

With 100 effective alternating volts impressed upon this combination of asymmetrical cells, known as the Graetz rectifier arrangement, a pressure of approximately 121 volts is observed by either direct or alternating voltmeters, the theoretical value being 141.4 volts. All these pressures are represented in Figs. 3 and 4, referred to the terminals *a* and *o* respectively.

The pressures obtainable from a double-current generator correspond to these condenser pressures. As is well known, between the positive or negative brushes (see Fig. 10) and either of the

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collector rings, there may be obtained unidirectional pulsating pressures, the collector rings being positive to the negative brush, and negative to the positive brush. The middle point of an inductance coil placed across the alternating pressure terminals is at all times at a potential midway between the potentials of the constant pressure brushes and midway between the potentials of the alter-

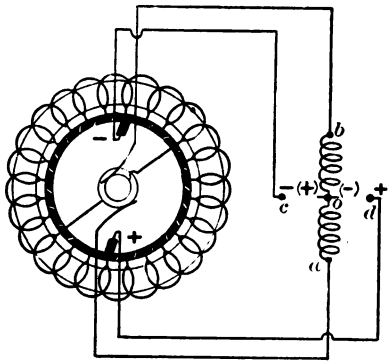

Fig. 10

nating pressure collector rings. Figs. 3 and 4 may represent the pressures obtainable from the double-current generators, as well as the pressures of the aluminum condenser.

VARIATION OF THE ENERGY WITHIN THE CELL.

The condenser action of this cell is to be found in the energy variations resulting from the variation of the distribution of the constant coulomb charge within the cell. The following discussion will illustrate the point:

Let E_m be the maximum value of the alternating pressure, and Q be the charge in coulombs which one of the films receives due to the potential difference F_m. The charge upon the second film is zero, as was shown previously, when the first film has its maximum charge.

The energy W_1 stored up in the condenser at the instant of maximum pressure is

$$W_1 = \tfrac{1}{2} QE_m$$

When the impressed pressure passes through zero, each film holds

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one-half the charge, at one-half the pressure E_m and the energy W_2 stored up in the condenser is

$$W_2 = 2\left(\tfrac{1}{2} \times \frac{Q}{2} \times \frac{E_m}{2}\right) = \tfrac{1}{4} QE_m$$

or *one-half* as much as at the time of maximum pressure. The pressure variation is

$$W_1 - W_2 = \tfrac{1}{2} QE_m - \tfrac{1}{4} QE_m = \tfrac{1}{4} QE_m$$

which is also one-half the total energy stored up when the impressed pressure is at its maximum.

COMPARISON WITH TIN-FOIL CONDENSERS.

Since, with a sinusoidal pressure wave impressed, the pressures upon the two dielectrics have been shown to vary sinusoidally, it follows that the condenser charging current is sinusoidal and likewise the energy variations in the circuit. The aluminum condenser thus has the same condenser effect upon a circuit that an ordinary tin-foil condenser has.

An aluminum condenser periodically absorbs and returns only one-half the total amount of energy it stores up. This charge is held upon one film only at the time of maximum charge. Consequently the effective electrostatic capacity of a condenser, as figured from its sinusoidal charging current, is but one-half the electrostatic capacity of one of its films. A tin-foil condenser absorbs and returns its total energy charge and its charging current is proportional to the full electrostatic capacity of its film.

In a certain sense the aluminum condenser may be considered to be like two tin-foil condensers of equal capacities placed in series, for the pressures upon each film have an alternating component equal to one-half the alternating pressure upon the condenser, and again, the effective electrostatic capacity of an aluminum condenser is one-half the electrostatic capacity of either film. However, each film of the aluminum condenser is subjected to nearly the maximum pressure upon the cell instead of but one-half the maximum as in the ordinary condensers; and either film becomes charged while the other becomes discharged, instead of being charged and discharged together as in the tin-foil components.

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The charging current of both aluminum and tin-foil condensers is a function not only of the pressure and fundamental frequency of the impressed pressure wave, but a function of the irregularities or higher harmonics in the pressure wave as well. Fig. 11 shows

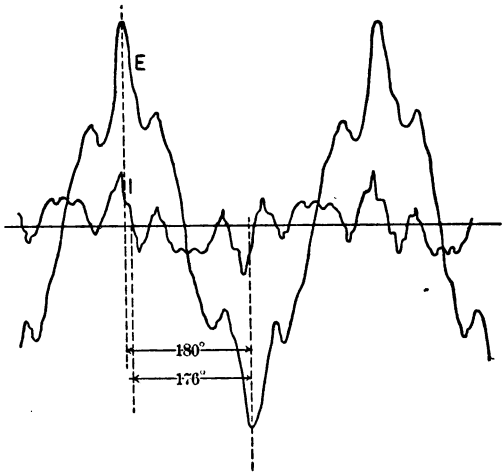

Fig. 11. CHARGING CURRENT PRODUCED BY IRREGULAR PRESSURE

the amplification of the charging current I produced in an aluminum condenser by the irregular pressure wave E. At each of the maxima and minima in the pressure wave, the condenser current passes through zero, for at these instants, the rate of change of the pressure is zero. The current is greatest where the wave is the steepest, *i. e.*, where the rate of change of the pressure is greatest. The effective value of the current, as measured by a Hoyt instrument, was 2.4 times the value calculated for a sinusoidal pressure wave of an equal impressed pressure (114 volts) and a frequency of the fundamental wave (60 p. p. s.). The condenser upon which these curves were observed had a capacity equivalent to a 40 microfarad tin-foil condenser.

THE LOSSES IN THE ALUMINUM CELL.

The losses of the aluminum cell consist of the following:

1. Film losses.
2. C^2R losses.
3. Electrolytic decomposition losses.

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The film losses are the principal losses in the cell and they include (a) leakage losses and (b) a loss proportional to the frequency. The leakage losses are due to minute local break-downs of the films and to an apparently uniform passage of current through the high resistance film by conduction. These losses (those due to the minute punctures of the film in particular) increase rapidly when the pressure upon a given film goes beyond a certain point which has been termed the "break-down" point. The point of break-down is dependent largely upon the kind and temperature of the electrolyte as well as upon the thickness of the film. By obtaining suitable conditions the writer has recently succeeded in operating simple two-electrode condensers directly upon effective alternating pressures, as high as 1,250 volts, without disrupting the dielectrics.

The losses proportional to the frequency are of a nature not yet clearly understood. With the higher commercial frequencies (60 to 130 cycles per second) they are in general greater than the other losses in the cell.

The C^2R losses of the electrolyte may be reduced to a negligible quantity by intermeshing sheet electrodes of opposite polarity. The electrostatic capacity per unit of surface is, fortunately, not so great as to cause the current density to be high. The enormous capacities per unit of surface in the so-called "polarization condensers" is one of their inherent practical disadvantages.

The losses caused by electrolytic decomposition are those due to the leakage current only. The wattless condenser current is induced in the electrolyte electrostatically. The products of decomposition may be made to consist chiefly of minute quantities of hydrogen and oxygen.

The presence of a break-down point in the aluminum cell, at which the losses begin to rapidly increase, is a particularly valuable property of the aluminum condenser, because the dangerous temporary rises in voltage that tend to occur through resonance are thereby practically prevented.

It is not of any serious consequence to scratch the electrode, for any break in the film is quickly repaired by electrochemical oxidization. Punctures due to abnormally high voltages are for the same reason of little consequence unless the puncturing be long continued.

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In general it may be stated that the voltage limit for single cells is not much above 150 volts where high efficiencies are desired. The efficiencies may range from less than 93 per cent. to as high as 97 per cent. according to the operating conditions It is possible to operate condensers continuously at efficiencies above 95 per cent. with pressures of 110 volts.

The weight, volume and cost per microfarad of single cell electrolytic condensers are considerably smaller than for equivalent tin-foil condensers operating at the same voltages. This great difference is not so marked where the voltages rise much beyond those at which single condensers can operate efficiently, since the energy storing value of a condenser varies as the square of the pressure upon its terminals.

The electrostatic capacity of 110-volt aluminum condensers may be said to be roughly ¼ to ½ microfarad per square inch of aluminum plate in the cell.

In applied electricity there is, evidently, a place for the aluminum electrolytic condenser.

SUMMARY.

The following are the principal points brought out in this paper:

The film coating the aluminum electrode varies from less than 0.000005 centimeters to more than 0.000050 centimeters as estimated by the interference color phenomena observed; this thin film acts as an asymmetrical dielectric as well as an asymmetrical conductor; a condenser with two of these asymmetrical dielectrics holds a constant coulomb charge when operating upon an alternating current circuit; this constant charge sets up a uniform pressure between the electrolyte and a point in the metallic or external circuit which is neutral to the alternating pressure; the pressures upon the films are uni-directional pressures which pulsate in continuous sinusoidal variations with one-half the amplitude and one-half the frequency of the pulsations of the impressed pressure; with the Graetz rectifier group of cells, uniform pressures of approximately 1.2 times the impressed alternating pressure may be observed; the condenser action of the cell is due to the energy variations accompanying the variations of the distribution of the constant coulomb charge within the cell; the energy varia-

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tions are one-half the maximum energy held by the cell; the ordinary condenser behavior upon AC circuits is possessed by the aluminum condenser; the losses in the cell are small and consist of film losses, C^2R losses and decomposition losses, the film losses being due to leakage and to a loss directly proportional to the frequency.

The writer hopes to continue this subject at later meetings of the Society, taking up among other points, the properties of the aluminum cell as shown by curves and other quantitative measurements; the peculiarities of cells having electrodes with films of different electrostatic capacities; and polyphase condensers, with their relation to polyphase asymmetrical rectifiers.

In concluding, the writer wishes to express his deep feeling of obligation to the electrochemical and electrical departments of the University of Wisconsin, whose instructional forces and whose laboratory equipments enabled him to take up the investigation of the aluminum condenser under most favorable surroundings. To Prof. C. F. Burgess in particular is he deeply indebted for inspiration and suggestions received. The thanks of the writer are tendered to Messrs. W. R. Mott and J. G. Zimmerman for their co-operation and assistance in some of the work, and to Mr. Budd Frankerfield for suggestions relative to the treatment of the subject in this and future papers.

University of Wisconsin.

DISCUSSION.

Mr. Mott: Aluminum foil is used as anode in dilute sulphuric acid, and the film of basic sulphate forms as on any aluminum anode. The metallic aluminum may be used up so completely that the film becomes transparent. A film formed in this manner is shown on this watch glass. It is easily analyzed and its absolute thickness can be determined. We will pass it around for inspection. A specimen of the aluminum foil is also here; and on this watch glass is a film of aluminum foil that has been oxidized in a Bunsen flame. This film is quite transparent, yet some metallic

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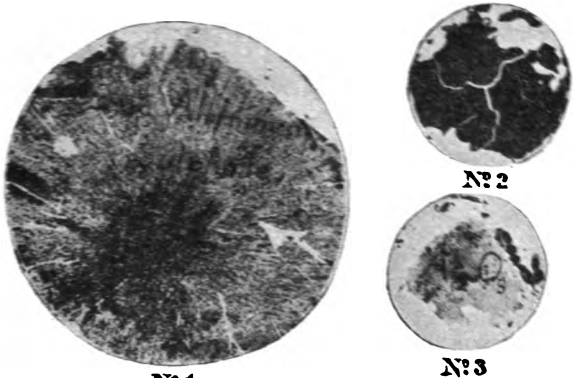
aluminum is still present. The aluminum becomes so thin (much less than a wave length of light) that it becomes transparent. The presence of aluminum is proved by the facts that this oxidized foil can be burnt to a crisp: it conducts electricity, and it has the appearance and lustre of aluminum.



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I wish to emphasize one vital factor in this problem. It is the great difference in thickness of the dielectric film as formed at different voltages. The thickness is, roughly, a linear function of the maximum voltage used; further, a film formed in sulphuric acid at 20 volts has a thickness greater than one formed in sodium acid phosphate at 100 volts; hence we see the history of the aluminum plates is of extraordinary importance. To get a true test of the capacity at different voltages we should form our films at those voltages as well as at higher voltages. I have here a few questions which are given by the way of suggestion. They are these: What effect does the previous use of the aluminum condenser at different voltages have upon its total capacity and its energy losses? For example, a newly set-up aluminum condenser is first used on a 20-volt circuit and then on a 100-volt circuit, and again on a 20-volt circuit. How closely will the two capacity measurements made at 20 volts compare? How much temporary difference and permanent difference would we find in the total capacity and in the angle of lead? We would also ask the same questions as to the effect of changing the electrolyte, but using the same aluminum plates. Finally, what experiments

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were made to trace the effect of impurities in the electrolyte upon the efficiency?

Mr. Zimmerman has referred to some of the earlier work upon aluminum anodes, and in this connection he called the aluminum electrolytic rectifier the Graetz rectifier. As Americans, I think we can object to this. Graetz was by no means the first. The priority of Bottome, here in America, and of Hutin and Le Blanc in France, over that of Pollak and Graetz, has not been so generally accepted because not so generally known. I have here one of Bottome's patents. It was taken out in 1891.

Mr. Zimmerman refers to my thesis on aluminum in regard to the dielectric constant of the film. Further experiments, by different methods, upon the thickness of the film in different electrolytes have since convinced me that a dielectric constant of 10 is fairly satisfactory.

As to the commercial possibilities of the aluminum electrolytic condenser, discussion would have been of interest. This condenser of great capacity is certainly more than a scientific toy. While, at present, the great electrical companies of this country are not commercially (openly) pushing the aluminum electrolytic condenser, yet the firm of Siemens & Halske have within the last few years taken out several patents upon it. This is certainly significant. The editor of the *Electrical World and Engineer,* in commenting on an article by Trowbridge and Westcott, suggests the use of the electrolytic condenser in telephony; and in view of the high efficiency obtained by Mr. Zimmerman over that of previous experimenters, we may expect the use of this aluminum electrolytic condenser as a "phase splitter," and again on the other hand, to balance self-induction of transmission lines, etc., etc. Numerous laboratory uses have been made of this condenser, such as its use with the talking arc (Mitkiewicz) and induction coils (Nodon). Being a cheap substitute for the tin-foil condenser, it is not unlikely that many other uses will be found. The use of this condenser with the aluminum rectifier is of interest.

This diagram[1] (Fig. 1) illustrates this use. Four electrolytic valves (A, B, C, D) are arranged as in Bottome's patents. By this arrangement, we obtain the alternating current A (Fig. 2),

[1] This is M. Nodon's method, and is described and figured by M. Montpellier: "L'Électricien" (Paris), vol. 23, page 401, June 28, 1902.

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rectified to B (Fig. 2). This current flows always from X to Y. In parallel with the circuit XY is placed the aluminum condenser

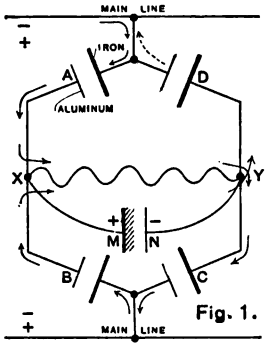


Fig. 1.

NODON'S ARRANGMENT OF ALUMINUM ELECTROLYTIC RECTIFIERS (A,B,C, & D) WITH AN ALUMINUM ELECTROLYTIC CONDENSER (MN.)

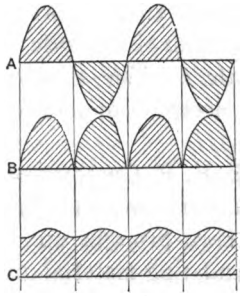
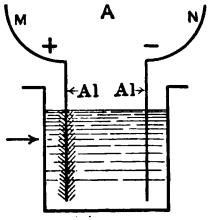


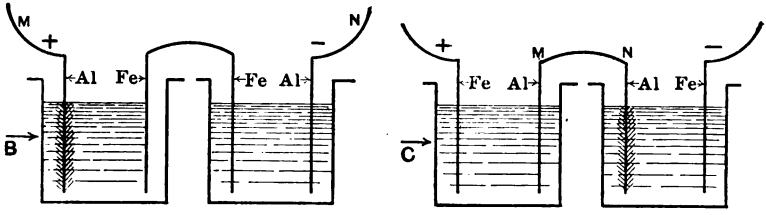
Fig. 2.

MN. This changes the rectified current B (Fig. 2) to C (Fig. 2), which is now suitable for circuits with large self-induction. For example, the field windings of an alternator might be supplied with this current. So the possibilities of this condenser are seen to be very attractive to inventors and engineers.

MR. SADTLER: I do not quite understand the difference between a condenser and a rectifier.

MR. MOTT: An aluminum electrolytic condenser consists of two





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aluminum plates which may be placed in one cell (A in diagram) or in two cells (B or C in diagram). The one-cell arrangement has the same capacity as the two-cell for like areas of aluminum surface. The two-cell arrangement of the condenser is essentially two aluminum electrolytic rectifiers in opposition. The aluminum electrolytic rectifier consists of a single aluminum plate and another electrode of indifferent material, such as carbon, lead or iron.

MR. E. E. F. CREIGHTON: I was not here during the first part of the discussion, and perhaps the point I have in mind has already been brought up. The question is that of the thickness of the insulating material on the surface of the aluminum. It does not seem reasonable to suppose that a thickness of insulation measured in millionths of a centimeter would be sufficient to withstand the voltage that has been put upon it. I would like to ask if measurements have been made of the drop of potential very close to the plate, and if the liquid itself near the surface of the plate may not be a part of the insulation.

MR. MOTT: The experiments of Fessenden and his students proved that the drop in potential and the formation of the leading current takes place within a few thousandths of the aluminum plate. Mechanical difficulties prevented work closer to the aluminum electrode.

On the thickness of the film that forms on aluminum anodes, I would add that it is clearly and exactly defined by the color phenomena. The increase in voltage required to pass through one spectrum can be accurately determined and is, perhaps, the best method of comparing the dimensions of the films formed under various conditions.

MR. CREIGHTON: It is so anomalous that a dielectric film, so thin and in contact with a liquid, should withstand such a great difference of potential, that it seems as though we should look beneath the film for a layer of dielectric which would be in series with the one measured. Possibly such a dielectric could be formed by a combination of the gas given off with the metal.

DR. GUTHE: I am very glad to hear that the presence of gas is proposed as being active in producing this high resistance; in fact, I have found the gas (oxygen) in the film. I think the film of oxide or hydroxide that is ordinarily given as being the source

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of the resistance in an electrolytic rectifier, and which breaks down as supposed, is not the only substance that we find on the plate; but we find, also, gas; and you can prove it by forming the film on the plate, then exhausting, and you will see the gas come from the plate in minute bubbles.

MR. MOTT: I would like to ask Dr. Guthe if he analyzed the gas as it came off. Aluminum in a vacuum is attacked by sulphuric acid; and we would like to know as to the analysis that was made of the gas.

DR. GUTHE: I did not understand the first part.

MR. MOTT: We would like to know as to the chemical analysis of the gas that came off. It is a well-known fact that aluminum in sulphuric acid in a vacuum is attacked more readily than it is at ordinary pressure.

DR. GUTHE: I had aluminum in the sulphuric acid.

MR. MOTT: What analysis of the gas?

DR. GUTHE: I have not made any analysis of gas.

MR. MOTT: You are not certain as to the gas?

DR. GUTHE: I am not certain that it is oxygen.

MR. MOTT: You are not certain whether it comes from the corrosion of the aluminum or from the storing up of gas in the film on the aluminum anode?

DR. GUTHE: Well, no, I cannot tell that; because I have not made a chemical analysis. It came right off from the plate in the ordinary solution. No acid was present.

MR. CREIGHTON: Sometimes the vacuum will not bring off all occluded gases in the metal. I am unable to say if it is so in this case or not. I know that in the case of iron I have had occluded or combined gases with the iron that it was impossible to get rid of by combined vacuum and heat treatment.

DR. GUTHE: One more point, after the gas had been produced the resistance of the film was very small, but it took only a very short time to increase the resistance again to its original value, while the formation of a similar resistance on a new plate would require a much longer time.

PRESIDENT RICHARDS: Might that not point to the fact that if the condenser were operated under pressure the resistance might be still higher?

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MR. MACNUTT: I would like to ask what the inductivity of the film is supposed to be.

MR. MOTT: The inductivity?

MR. MACNUTT: Yes, the inductivity of the dielectric.

MR. MOTT: In earlier discussion, a value of about 10 was considered satisfactory.

MR. MACNUTT: About 10?

MR. MOTT: Yes, I think that would be a value to be expected in a film of this chemical composition (a basic salt).

DR. R. GAHL: I should like to ask whether somebody has had experience about the constancy of such aluminum cells used as condensers. I tried once to use aluminum cells as condensers in measurements of the resistance of storage cells. For such measurements wire resistances cannot be used, because the cell would discharge through them; so it is necessary to measure with alternating current and use condensers instead of resistances. But the capacities of the condensers proved to be very inconstant; and I should like to know whether there is perhaps a chemical which can be used as electrolyte for aluminum cells which makes them constant enough for such measurements.

MR. CREIGHTON: That brings up the point of leakage in these cells about which I think Mr. Mott might give us considerable information. I understand that ordinarily there is a very appreciable leakage of current.

MR. MOTT: The leakage of current is not large at moderate voltages in electrolytes like phosphates, citric acid, etc., but as you approach the critical voltage, the film breaks down under the dielectric strain and minute sparks can be readily seen under the microscope. The leakage loss now rises rapidly.

DR. GAHL: As a matter of fact, I would observe that I only tried to use aluminum cells for a voltage of about 2 volts; and I found they did not nearly keep their capacity for the time involved in these measurements.

MR. MOTT: Mr. Zimmerman has a lot of experimental data, very carefully obtained, to found his statements upon, and a look over the literature will show that Mr. Zimmerman's paper is much superior to anything previously attempted in regard to aluminum electrolytic condensers.

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DISCUSSION.

(Communicated.)

MR. MOTT: The following quotation from Weeren[1] is so explicit about the ready solubility of aluminum in nitric acid and dilute sulphuric acid under diminished pressure that perhaps it is pardonable to give the quotation exactly and in the original German.

"Die hier mitgetheilten Thatsachen dürften einiges Interesse beanspruchen, da sie nicht nur beim Zink und verdünnter Schwefelsäure obwalten. Aehnliche Resultate wurden auch beim Cadmium, Cobalt, Nickel, Eisen und Aluminium erhalten. Das Aluminium, welches sonst von verdünnter Schwefelsäure und Salpetersäure kaum oder gar nicht angegriffen wird, löste sich im Vacuum in jeder dieser beiden Säuren ziemlich leicht. Ebenso löste es sich in einer vollkommen neutralen Eisenchloridlösung im Vacuum ziemlich leicht, indem es die Eisenchloridlösung unter Wasserstoffentwicklung zu Eisenchlorür reducirte; bei gewöhlichem Luftdruke ging dieser Process sehr viel langsamer vor sich. Aehnliche Beispiele würden sich noch viele finden."

Since the close of the Washington meeting, I have repeated some of the experiments of Weeren and of Guthe. For this purpose, I used suction flasks containing dilute sulphuric acid (sp. gr. 1.060) and aluminum plates. A hydraulic air-pump served very well for reducing the pressure. The evolution of gas from the aluminum was vigorous under diminished pressure, but very slight under atmospheric pressure. After twenty-four hours, the reaction under diminished pressure seemed as vigorous as at the start. This experiment can be set up in a very few minutes.

The idea that the gas entangled in the film is going to relieve the film of the dielectric strain is not of so much value when you consider that a continuous support must be furnished by the film to withstand the large forces of compression due to the enormous charges on the two sides of this extremely thin film. The supporting cellular structure which Guthe pictures, must stand the whole force of the dielectric strain under any circumstance.

Again, the dependence of the critical voltage on the composition of the film is very great. A film formed on aluminum in a sul-

[1] Berichte der deutschen chem. Gesellschaft, Vol. 24a, page 1785, June 8, 1891.

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phate solution will stand an electrical pressure of from 20 volts at ordinary room temperature to 50 volts at zero degrees. Films formed by chromate, hydroxide and carbonate solutions have critical voltages near 100 volts. Tartrates and a multitude of organic acids and salts, phosphates, etc., give higher critical voltages (near 200 volts). Citric acid and a few other organic acids give critical voltages that sometimes exceed 500 volts. A critical voltage of 1,250 volts has been found by Mr. Zimmerman for one electrolyte. These facts and those already mentioned about the thickness of the film convince one that the chemical composition is the important factor.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904, President Richards in the Chair.

A CONTRIBUTION TO THE STUDY OF THE ELECTRIC ARC

By William S. Weedon.

Arcs may be roughly classified into

I. Crater arcs.

II. Flame arcs.

To the former class belong the plain carbon arc and arcs between certain conductors of the second class, such as zirconium oxide (Rasch arc). To the latter class belong the so-called flame carbon arcs (*e. g.*, Bremer arc), which are drawn from carbons containing certain metallic salts; we also have in this class the arcs from most metals. In the first class the light obtained is derived principally from the two spots or craters, while in the second the arc stream itself furnishes the greater part of the light—generally all. This second class offers by far more interesting study, since we are able to follow the changes in the character of the light as we alter our conditions.

Only direct current arcs are considered in this paper, the source of current being a 500-volt generator, and in some cases the Edison three-wire circuit for 125 and 250 volts.

The relations between voltage, current and arc length are fairly well known, but for the sake of illustration I have given two sets of curves for the iron arc, and in general form these curves apply to both classes of arcs. The measurements are across the arc terminals.

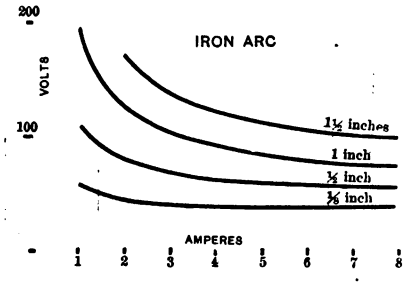

FIG. 1.

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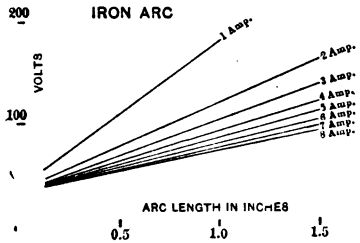

FIG. 2.

One of the most important problems in connection with the arc is with reference to the amount of material which is transported during the running of the arc. In the air, for most materials, this is quite large. The rate of waste of carbon is diminished by running "enclosed," or in an atmosphere of carbon monoxide. The question is, how much material is necessarily transported at given current density, voltage and arc length? Is there any law for arcs corresponding to Faraday's law for solution?

First of all, it is evident that the heat conductivity of the electrode is an important consideration, as it is plain to one who is at all familiar with the arc that there is much more material volatilized by heat than is necessary to furnish material for the active part of the arc.

Copper arc in air.

The following experiments will give a good idea of the relation between the number of ampères used and the rate of waste, and also shows the tendency for the anode to gain in weight rather than lose.

Two arcs were run in series, both being vertical in order to obtain conditions as uniform as possible. Only the lower electrodes were weighed. In both arcs the electrodes were ¼ inch

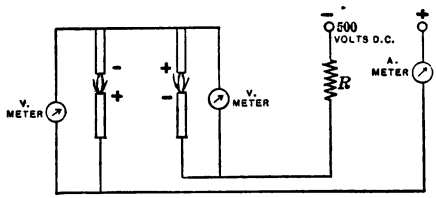

FIG. 3.

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in diameter; arc length, $\frac{1}{8}$ inch; time of running, two hours, at 2 ampères, 45 volts.

	Cathode. Grams.	Anode. Grams.
Weight before running	20.610	20.821
Weight after running	20.288	20.833
Loss	0.322	...
Gain	...	0.012

Upon increasing the current to 5 ampères at 35 volts (same arc length) and running for two hours, the result was as follows:

	Cathode. Grams.	Anode. Grams.
Weight before running	20.247	20.764
Weight after running	18.462	20.833
Loss	1.785	...
Gain	...	0.069

In the latter experiment, the current used is 2.5 times as large as in the first experiment, but the loss in weight of the cathode is more than five times as great.

A fact to be noted here is the tendency for the heavy, outer mantle of the copper arc to appear only occasionally when the current is low. This is undoubtedly connected with oxidation, and the same phenomenon is to be seen in iron arcs. In Fig. 4 (*a*), the arc is shown with the outer mantle invisible; when the

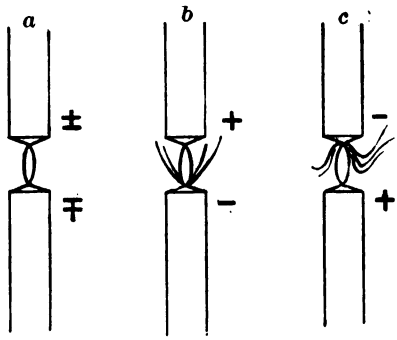

FIG. 4.

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outer mantle flashes, it appears to come from the cathode, as is represented in (*b*) and (*c*).

Cooling the electrodes was then tried, the arrangement being as before. The lower electrodes, however, which were weighed, had the form of a copper shell, ¾ inch in diameter, 1¼ inches long and 1-64-inch thick. The upper electrodes were the same as before. Water was sent in a jet against the tip, as is shown in the sketch.

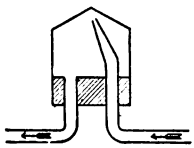

FIG. 5.

While the arc was running, the lower electrodes could be touched very close to the arc without any sensation of warmth being experienced. The result of several experiments is as follows:

Time, 1½ hours; current, 2 ampères; volts, 50. The arc length was somewhat more than ⅛ inch, as it was found that with ⅛-inch arc an arc of rather different color—purplish—was obtained in the case where the cathode was cooled. Under these conditions neither electrode lost in weight, and the gain was apparently due to oxidation.

	Cathode. Grams.	Anode. Grams.
Weight before running	13.014	12.649
Weight after running	13.018	12.672
Gain	0.004	0.023

In order to determine the actual loss of the cathode it was reduced in hydrogen, and the real loss found to be 0.013 gram. It is to be seen from this that the Faraday equivalent, if one exists, does not apply to arcs as it does to solutions, since by this amount of current, 450 times the amount of copper should have been transferred.

In order to overcome the influence due to oxidation, it was determined to run an arc in nitrogen between copper electrodes.

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The general results, however, were exactly the same as when the arc was run in air, and it appears that the copper and nitrogen undergo combination under these conditions. The arrangement used is shown in the following sketch:

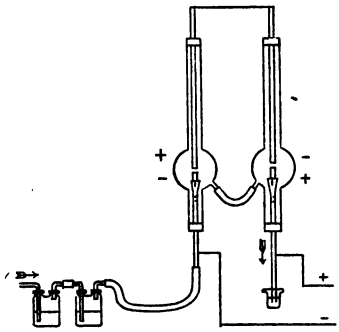

FIG. 6.

The gas was generated in the usual way from sodium nitrite and ammonium chloride, and purified by passing through aqueous potash and concentrated sulphuric acid.

Copper arc in hydrogen.

In some preliminary experiments, the vertical arc was used with cathode below, the electrodes being solid ¼ inch copper rods. With the 500-volt circuit only a short arc could be drawn, and the cathode was found to lose in weight, while the positive electrode gained. By varying the arc length and current three distinct kinds of arc were obtained.

1. When the electrodes are cold, at the starting of the arc, with about 1,300 ohms in series, there occurs momentarily a discharge giving a pink glow, which soon changes to one of the arcs described below. The spectroscope shows strong hydrogen lines.

2. An arc of about ⅛ inch in length, current 0.5 ampère, voltage about 300. The arc is non-luminous, shows both copper and hydrogen lines to a slight extent. There is a faint glow around the positive electrode, arranged in transverse striations. The negative electrode is hotter than the positive, and the discharge is irregular, seeming to come from a small point on the positive to a much larger and brighter spot on the negative electrode.

3. While arc No. 2 is being run, if the series resistance is

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decreased by about 100 ohms, at a critical point, a green copper arc suddenly appears. Hydrogen lines, as well as copper lines, may be seen, but frequently only the copper can be detected.

The voltage has dropped from 300 to about 70 during this change, and the current rises to 4 ampères. The discharge is quite irregular.

A single bulb was used for these arcs, the arc being arranged as was shown in the case of the copper arc in nitrogen. (Fig. 6.)

A curious phenomenon was observed here, and in order better to study it the arc was placed horizontally. The two electrodes were of the same size, held by adapters. The negative was seen to be much hotter than the positive electrode and soon became molten over the tip. While the arc was running, nothing peculiar was observed, but as soon as the circuit was broken, or when the arc went out of its own accord, the molten copper swelled suddenly to two or three times its normal size. It often happened that, when the arc went out of its own accord, the space between the electrodes was bridged over and the arc started anew, the phenomenon occurring many times. It appears that this is due to absorption of hydrogen, which is given off at the temperature of the arc.

Water-cooled electrodes were now tried, a single horizontal arc being used and arranged as shown in the sketch.

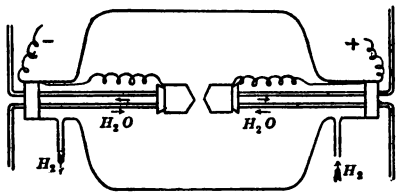

FIG. 7.

The bulb was about 8 inches long by 6 inches in diameter, with the main tubes 1 inch in diameter. The arc was drawn by pushing the stoppers in the tubes and then withdrawing them. In this experiment, the current used was only 0.35 ampère; the arc length was quite short, 1-32 inch or less, and the character of the arc was not allowed to change from the non-luminous arc above described as arc No. 2. The time of running was 1½ hours.

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	Cathode. Grams.	Anode. Grams.
Weight before running	12.657	12.185
Weight after running	12.653	12.189
Loss	0.004	...
Gain	...	0.004

Although the loss and gain in weight is very small, and the experimental error possibly large, it is certain that we have obtained a smaller loss than ever before, and if the figures are within any degree accurate there is transferred only about 1/1500 of the Faraday equivalent for solution. The spot upon the cathode was in this case also larger and brighter than upon the anode.

Arons* attempted to obtain the copper arc in hydrogen with electrodes separated 0.1 mm. He used only 106 volts, however, and consequently was unable to obtain an arc. He also states that at 65 mm. pressure he had considerable difficulty in obtaining a discharge between iron electrodes in hydrogen. This was therefore tried with the 500-volt circuit, and under the same conditions previously given for the copper arc.

Iron arc in hydrogen.

When solid iron rods are used, the same pink light, described under copper arcs, was obtained. This changed almost immediately to a high voltage, non-luminous arc discharge, but it was impossible to obtain a true iron arc before the electrodes were completely melted down.

Water-cooled shells were employed, as described for the copper arc. The arc was run three hours, with current 0.35 ampère, voltage about 300. The spot upon the cathode was larger than that on the anode. Apparently the running of the arc under these conditions is not perfectly simple, and it seems probable that some combination with hydrogen takes place; the iron blackened around the large spot on the cathode, and beyond this, and also on the anode, there appeared curious bronze-like colorations. In several experiments, run under the above conditions, the anode lost in weight and the cathode gained. This amount varied from .003 to .005 grams, according to the circulation of the water. Low as these changes in weight are, I feel sure that the experimental

* Annalen der Physik (1900), 713.

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error is not large enough to allow the possibility of the change in weight being in the other direction.

Carbon arc in hydrogen.

Carbons ¼ inch in diameter were used, the arc being placed horizontally, and the electrodes being held by adapters. At 2 ampères an arc 3-16 inch in length registered 180 volts. The light was not brilliant, the arc stream itself being non-luminous and appearing as a fine line connecting the two electrodes.

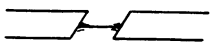

FIG. 8.

The temperature of the two electrodes seemed to be about the same, nor could it be said with certainty that any difference in size of the two craters was noticeable. The presence of acetylene or hydro-carbons of the acetylene series was shown by passing the exhaust hydrogen through an ammoniacal solution of cuprous chloride. A very slight brown precipitate was formed. The arc was run for two hours, and the result was as follows:

	Cathode. Grams.	Anode. Grams.
Weight before running	3.513	3.405
Weight after running	3.440	3.278
Loss	0.073	0.127

Under the microscope, the negative after running showed its surface to be covered with small pits, which were distributed with fair regularity, while the positive showed larger depressions distributed with less regularity. The spectrum observed was a combination of the enclosed arc spectrum and the hydrogen spectrum.

It seems that oxidation, or combination with the surrounding gas, is not absolutely necessary for the production of a metallic luminous arc, but such combination facilitates its formation. This was further confirmed by some experiments made with metallic chromium at 1 mm. air pressure. At low current a Geissler discharge was obtained, but at higher current the true chromium arc appeared.

With regard to the amount of material fed to the arc it may be

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said that there is apparently a tendency for the arc to ionize the surrounding atmosphere if there is not enough material vaporized from the electrode. If much heat is developed, more is vaporized than is employed in transporting the current. Between these two extremes both the atmosphere and the electrode vapor are ionized. We can therefore hardly make measurements which will give us figures comparable to Faraday equivalents. It would appear from this that there is a slow gradation from the spark discharge to the true arc, passing through the intermediate stage where both kinds of discharge are present. The main distinction, therefore, between the arc and the spark discharge is, that in the former vaporized material from the electrode or electrodes undergoes most of the ionization which takes place, while in the latter the surrounding atmosphere suffers most of the ionization. Undoubtedly, as Prof. J. J. Thomson observes, in the arc discharge the terminals are incandescent, while such is not the case in a spark discharge; but it appears to the writer to be more a question of securing sufficient material vaporized from the electrodes (by heat or by current direction) which vapor can be ionized; for there is undoubtedly an extremely small quantity of the material transferred by the current itself.

In this we assume that when the copper spectrum appears, copper is undergoing ionization, and that when the hydrogen spectrum appears, hydrogen is undergoing ionization. This will be discussed later.

Structure of arcs.

The structure of metallic arcs in air is in general, as follows:

The very middle path is not luminous, but the light is derived from the outer mantle, and most frequently from that portion of the outer mantle next the inner path, as represented in Fig 9. In the carbon arc the outer mantle is not well defined, owing to the fact that the product of combustion is gaseous.

It seems probable that the inner non-luminous path above mentioned is in a way comparable to the Crookes' dark space. The explanation given for the presence of the latter is that the large number of negative ions present have too great a velocity to ionize the atoms with which they collide, but that farther along the tube, when their force has been diminished by collision, ionization may take place. Where this occurs light is given off.

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In the arc, the inner path may be caused by the fact that the negative ions in very great number, are moving rapidly toward the anode, and producing ionization only where their force has been sufficiently diminished by collision, viz., on the sides of the inner path.

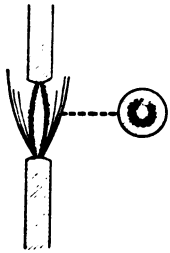

FIG. 9.

There are many changes in the character of an arc during running which are very subtle and of rather obscure origin. In many instances the material depositing on one or both electrodes causes difficulty, and in many instances irregularity in the composition of the material used causes unexpected alterations in the structure of the arc.

Does the cathode determine the character of the arc?

In studying the characteristics of the arc, the first fact which one is apt to discover is that the light given off by an arc is not produced by simple heating of particles present in the arc. The opinion was held by the writer for some time, and arrived at after a number of experiments on metallic arcs, that the cathode determines the character of the arc. But here (as in a number of other experiences in the study of the arc) some incorrigible facts appeared just as the opinion was well established, and made the generalization impossible.

There are cases in which the cathode does not appear to be the determining feature. For instance, two very clear and conflicting cases are as follows:

Copper cathode and magnetite anode give copper arc.

Magnetite cathode and copper anode give iron arc.

Here the cathode undoubtedly determines the nature of the arc.

Copper cathode and thorium carbide anode give thorium arc.

Thorium carbide cathode and copper anode give copper arc.

Here we have the anode giving character to the arc.

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Besides these contradictory cases we have such substances as tungsten, calcium carbide and zirconium carbide, acting almost as well in one direction as in the other when copper is used as the second electrode. The conditions for the above experiments were in each case as follows: Diameter of electrode, ½ inch; arc length, 1 inch; current, 3 ampères; voltage, about 100. It is well to give exact conditions in these experiments, as some arcs do not behave the same under conditions which are varied only slightly. This may be illustrated by the magnetite-copper arc above described. A vertical arc is used with the magnetite as cathode below. Under the conditions above given with regard to current and arc length, no copper appears in the arc at all. This is true, apparently, at all current strengths tried, from 1 ampère to 15 ampères. It does not seem to hold, however, below 0.5 ampère. If we start with 3 ampères for a 1-inch arc and gradually reduce the current by throwing in external resistance, the arc changes, as is shown.

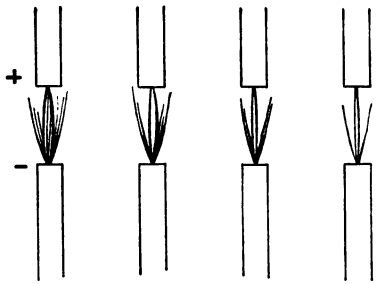

FIG. 10.

When the current reaches 0.5 ampère, however, the character of the arc suddenly changes, and instead of a pure iron arc we have one in which the copper is shown clearly around the anode.

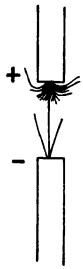

FIG. 11.

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Whether we are bordering upon the phenomena of spark discharge here or not, the arc characteristics certainly seem to be changed. Reduction in the supply of cathode material seems to be the most important factor. The copper appears to take a part in the ionization when the iron fails to be produced in quantity sufficient to feed the arc. The same phenomena above described may be seen if the copper as cathode is placed below, with the magnetite above. At low current the iron flashes out, and the spectrum of the upper portion is that of iron, while the lower portion is purely copper.

The position of the electrode materially alters the character of the arc. If an arc is drawn between two terminals of different composition, and the arc belongs to the class in which the cathode, rather than the anode, determines the arc characteristics, the arc flame is naturally fed more uniformly if the cathode is below. We then obtain an arc of clean-cut characteristics, showing generally the spectrum of the cathode only, and possessing a well-defined structure, composed of an inner path, the intermediate luminous path and the outer mantle, which may possess more or less luminosity. If the cathode be placed above, we have the material composing the cathode fed to the arc rather badly, for it does not extend, as a rule, completely across this space to the anode (1-inch arc being used). As a result, the upper portion of the arc possesses strongly one set of characteristics, while the lower portion partakes, to a greater or less extent, of the properties of the anode.

It certainly cannot be said that the cathode always determines the nature of the arc. There seems rather to be a kind of selective action taking place, some substances being ionized in preference to others. This is strongly brought out by a study which is at present being made in this laboratory of electrode mixtures. It is certainly true that metallic salts are ionized very readily in the arc, and the presence of carbon also has a peculiar effect. It is to be especially noted here that this ease of ionization does not depend altogether upon the volatility, nor even upon the mere presence of the vapor of the substance in the arc. The direction of the current may determine it in a given instance. If we take the example already used, of copper-magnetite with magnetite as anode below, the copper is certainly at a lower temperature than

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when the current is reversed, yet the arc is entirely a copper arc. No iron appears in the arc or its spectrum, even though the current is raised to 15 ampères, and the magnetite is boiling so strongly that the arc must be filled with its vapor. Why is not the vapor ionized, giving the iron arc? Why do not even the heated particles give off light?

In trying to gain some conception of what takes place in the arc, we must go back to the study of the distribution of potential in the arc stream. The potential gradient is about as follows:

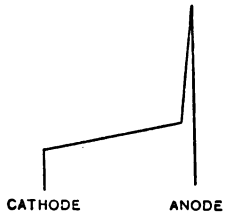

FIG. 12.

We ought also to have some conception of the process of ionization in the arc, and for this purpose I quote the views of Prof. J. J. Thomson, which were given in his lectures at the Johns Hopkins University last June.*

"On this view the cathode is bombarded by the positive ions which maintain its temperature at such a high value that negative corpuscles come out of the cathode; these, which carry by far the larger part of the arc discharge, bombard the anode and keep it at incandescence, they also ionize, either directly by collision or indirectly by heating the anode, the gas or vapor of the metal of which the anode is made, producing in this way the supply of positive ions which keep the cathode hot. It will be seen that the essential feature in the discharge is the hot cathode, as this has to supply the carriers of the greater part of the current in the arc; the anode has in general to be hot, otherwise it could not supply the positive ions which keep the cathode hot."

Prof. Thomson also gave as his opinion that the positive ions would ordinarily act as the principal current carriers, were the distribution of potential more regular; for there is generally more heat developed at the anode than at the cathode. The sharp drop

* See "Conduction of Electricity Through Gases," by Prof. J. J. Thomson, p. 424.

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of potential at the anode, however, acts as a barrier in the path of the positive ion.

It would appear from this that if this sharp drop of potential could be eliminated that the positive ions would lend character to the arc, as well as the negative ions. We should then have the character of the anode influencing the nature of the arc to a great extent. In order to test this, a large number of experiments were made, and the general results will be given.

Under certain conditions arcs have a tendency to hiss, and this is accompanied by several phenomena which are very interesting. In the first case, there is a diminution in voltage across the arc, and this generally amounts to about 10 volts, whatever the character of the arc. It has been shown that these 10 volts are lost principally by that portion of the arc next to the anode.*

From this it would seem that a hissing arc might offer a chance to test the idea advanced by Prof. Thomson, and some of our experiments seem to confirm the supposition, although it is difficult to obtain a case which is clearly defined.

The magnetite-copper arc is one of the clearest cases known. The copper, as cathode, is placed below. As has been frequently stated, the arc is distinctively a copper arc—under normal conditions. Hissing occasionally takes place, however (the noise is not a prominent feature except in carbon arcs), and a bright jet of flame appears at the anode. This flame is due to iron, as is shown by the spectroscope and by the color. The arc voltage was decreased by 10 volts during hissing, and an exploring rod of iron showed that these 10 volts were lost, for the most part at least, at the surface of the anode.

In this case, at least, it would appear that during hissing, the positive ions may carry a large part of the current, due to the lack of the potential barrier which is present in normal arcs. The electrodes in the above experiment had a diameter of from ¼ inch to ¾ inch, while the current varied from 3 to 7 ampères; arc length, ¼ inch to 1 inch.

Here, again, however, we are thrown somewhat in doubt, as this bright jet of flame from the anode often occurs when there is no drop of potential at all. This frequently occurs with such sub-

* Luggin, Wien. Sitz. 93, 1192.
Aryton, "The Electric Arc." p. 310.

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stances as ferro-manganese, which are capable of ready oxidation. Nevertheless, whenever this drop of 10 volts occurs the characteristics of the anode appear. We are forced to the conclusion that if the assumptions we have made are correct, there are times when the potential barrier, mentioned by Prof. Thomson, is not sufficient to hold the positive ions in check. This may be assumed also for those arcs in which the characteristics of the anode appear when running under normal conditions.

At any rate, it may be seen that the character of the light is not determined simply by the heated particles present in the arc. There certainly may be heated particles present which are not active in giving off light. It does not appear altogether out of the question to associate the light derived from the cathode with negatively-electrified particles, and that derived from the anode with positively-electrified particles. There seems no necessity for making a more complicated assumption, although we must admit that one may be possible. It is perfectly conceivable, for instance, that under certain circumstances the vapor from the anode may be ionized by negative ions, and consequently, should be associated with the latter.* The experiments above recorded with reference to the magnetite-copper arc do not seem to be in accord with this view, however.

Research Laboratory,
General Electric Co.

DISCUSSION.

MR. CREIGHTON: Several points came up in Dr. Weedon's paper that are of particular interest to me, about the ionization and that sudden flashing out that are noted at times without an apparent decrease in voltage. I would like to ask if Dr. Weedon made any oscillographic measurements of the voltage at that instant to ascertain if the voltage was perfectly stable. Since such

* **Townsend, Phil. Mag. (6), 1, p. 198 (1901), 3, p. 559 (1902).**
Townsend, Nature, 62, Aug., 1900, p. 340.
Townsend and Kirkby, Phil. Mag. (6). 1, p. 630 (1901).

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a high electromotive force is necessary in order to keep a stable arc, it would seem possible that a varied voltage might occur at the arc terminals, due to the difference in drop over the series resistance, and that the voltage at the terminals might vary in a very short time, not long enough to be indicated by an ordinary D. C. voltmeter, yet long enough to shoot out a little flame in the arc, which to the eye, would be permanent.

DR. W. S. WEEDON: No oscillographic measurements were made at all. It would be very interesting and probably important to make them.

MR. CREIGHTON: I should like to ask also if there was any work done on the occlusion of hydrogen by the copper. What was the appearance of the copper containing hydrogen when it was cold?

DR. WEEDON: Apparently the gas is occluded. After cooling, the large material was full of pores, and I may also remark that the color of this copper was whiter and the color of the transferred copper whiter than the copper with which we started the experiment.

MR. CREIGHTON: I understand that the nitrogen combined in some way with the metal and changed your weights.

DR. WEEDON: The weights could not be determined very accurately on account of some scaling of the copper; the experiments were discontinued, not only on this account, but on account of the fact that we were trying to find a neutral atmosphere and the measurements were simply made long enough to determine that the transfer of material was from cathode to anode. There was no swelling as in the case of hydrogen; and a darkening of the copper took place which may have been due to impurities in the nitrogen; that is, the presence of oxygen, because there was no special purification of nitrogen.

MR. CREIGHTON: It is not absolutely certain that there was combination between the nitrogen and the metal.

DR. WEEDON: I feel sure of it, because the arc was just as we have the arc in air. The outer mantle was distinctly visible; the voltage, under given conditions of current and arc length was the same, or very close to what it was in air, and I don't think a small trace of oxygen would have so great an effect.

MR. CREIGHTON: Why was the lower electrode weighed in preference to the upper electrode?

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DR. WEEDON: Because the lower electrode stands a better chance of being increased in weight by material which is transferred by the current alone, rather than by vaporization by heat from the other electrode. The upper and lower electrodes are not uniform with respect to their relation to the arc.

MR. ——: I would like to ask Mr. Weedon in the experiment in which he used water-cooled electrodes whether there was any great luminosity of flame; whether he made any candle-power measurements of that flame, and whether this is a case in which the electrodes had no loss in weight; and whether the flame was of sufficient magnitude to be used for illuminating purposes.

DR. WEEDON: There were no experiments made in which there were absolutely no losses in weight, although in this one instance to which you refer, where it was practically nothing, the arc possessed very little luminosity; and even though you raised it to the point where the luminous copper arc appeared, there was absolutely no possibility of making it a commercial source of light.

WM. HAND BROWNE, JR.: Is there any indication of a change in the characteristic of the arc at the surface of contact between the iron and copper vapors, due to an electromotive force there set up?

DR. WEEDON: I think that would be very difficult to measure. It probably could be done, though, by the use of exploring carbons; and yet with regard to the use of these I do not think they are very reliable. The thermo-electromotive force is probably very high, and in the use of an ordinary voltmeter experiments cannot be within a great degree accurate.

MR. CARL HERING: In order to draw any definite conclusions from these very interesting experiments it would be necessary to operate these arcs with a battery current, as distinguished from a dynamo current. I understand that the experiments were made with a 500-volt dynamo. It would be very difficult to construct such a dynamo which would not give a very fluctuating current; so that in the arc itself there must have existed periodically high and low voltages, and it is quite possible that some of the effects were due to the momentarily high voltages, and others to the momentarily low voltages. It seems quite likely that if a battery had been used his results would have been more uniform, and would have been more likely to have led to more definite conclu-

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sions. In place of a battery sufficiently large to run the arc, it might be possible to get a sufficiently steady voltage by connecting a small battery in multiple with the dynamo, so that the dynamo really furnishes the current while the battery acts as a sort of an equalizer, making the voltage curve more nearly horizontal.

DR. WEEDON: I think that Mr. Hering is undoubtedly right in that. There are so many unexpected variations in an arc that cannot in any other way, it seems to me, be explained, that work with a battery current would be very welcome. I may say that in most instances, however, the variations which we have in an arc from two electrodes which are different, is due not so much to the variation in current, but to the deposit upon the one electrode or the other—a deposit of oxidized material; and this may often cause alterations that will seriously disturb the working of the arc and especially the practical working of the arc. Under these circumstances we fail to reach a condition of equilibrium.

PRESIDENT RICHARDS: I was interested in noticing that Dr. Weedon states that it was impossible to obtain a true iron arc before the electrode was completely melted down; whereas the copper arc was obtained easily, before the electrodes were melted down. Since copper has a melting point about 500° C. less than iron, this must be due to the different heat conductivities of the copper and the iron, the iron melting because of its low heat conductivity, and the copper not melting because of its large heat conductivity taking heat away from the point of copper arc. The phenomenon of the swelling of the copper is, I think, familiar to those who have melted copper and have treated copper. It has the capacity of absorbing gases, just as iron has, and in giving them out at the moment when it sets; it is what we call the occlusion of the gases by the melted metal. It is a phenomenon just like air separating out of water when it freezes and becomes ice. Gases are absorbed in melted metal and are expelled sometimes with considerable violence as it sets; so that in steel works it is necessary, frequently, to stopper down the molds to keep the iron from boiling out by the evolution of the occluded gas. I think that is another phase of the same phenomenon which is met with in casting copper. Did Dr. Weedon observe any fuming or foaming up of the iron?

DR. WEEDON: I do not at the moment recall; but as well as I

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remember the iron did not swell in the same way as the copper. The occlusion of this gas in the copper has been noted, and the swelling, too; but I had no idea that it could be as large as it is. In comparison with the preparation of ammonium amalgam, it is of the same order. The literature on the hydrides of copper, however, is quite peculiar, and apparently this material is decomposed, according to some authors, at a much lower temperature than the temperature at which the swelling occurred; so that it may not be due to the formation of a copper hydride, but purely to the occlusion of gas by the copper.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904, President Richards in the Chair.

SOME PHENOMENA OBSERVED IN CONNECTION WITH THE USE OF A COPPER VOLTAMETER.

By Isaac Adams and Barry Mac Nutt.

Last summer the writers were engaged in the determination of the horizontal component of the earth's magnetic field by the tangent galvanometer-voltameter method. As it was desired to obtain results correct to within 0.1 per cent., great precautions were used to obtain reliable data, both in the care with which the observations were taken and in the accuracy of the instruments used.

Current was measured by a copper voltameter connected in series with a tangent galvanometer through a reversing switch, the object of the latter being to obtain reversals of the current through the galvanometer.

THE VOLTAMETER.

The copper voltameter consisted of a spiral electrolytic copper anode (or two flat plates) suspended in a vessel containing the copper sulphate. The removable cathode (platinum, or copper, plated on platinum) was hung within the spiral anode. The cathode had a connecting wire ending in a conical copper plug, which could be pressed into a conical hole in an arm of copper extending over the voltameter; good connections and rapid manipulation being thus insured.

The cathode, after a run, was washed in water, then in alcohol, dried with bibulous paper, held over an alcohol flame and gently warmed so that its temperature would not exceed 80° C. (being dried at this temperature the platinum quickly comes back to its original weight), then suspended in a closed vessel over sulphuric acid for twenty minutes, and weighed.

In the actual runs to determine H, the current was passed

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through a metallic circuit of equal resistance for a period of fifteen to twenty minutes, and at a given moment switched into the cell circuit, thus in a measure avoiding excessive polarization in the battery itself and consequently difficult readings.

The electrolyte used consisted of 100 grams of $CuSO_4$ dissolved in 1000 cc. of water, to which was added 1.5 cc. of H_2SO_4. In order to be sure that cuprous salts could at no time be present in the solution, the solution was heated now and then before use and kept constantly acidulated, and occasionally a fresh solution was made.

In some of the experiments a Weston milliammeter was used in series with the cell, but it was found that this instrument had an error of from 0.6 per cent. to 0.9 per cent. The care with which the observations were made and the close correspondence of the observations, together with the accuracy with which the galvanometer was constructed and its constant determined, gave results which are believed to be accurate within 0.1 per cent. The cathode was weighed upon a balance which weighs easily to 1/20 mg.

THE SOURCE OF CURRENT.

The cell used was the largest French Bunsen bichromate (immersed inner surface of zinc cylinder about 90 square inches), and its constancy for the strength of current used is shown by the following data which gives the deflection of the galvanometer for a current of about 0.19 ampère; the current flowing through a metallic circuit having approximately the same resistance as the electrolytic cell used. Readings were taken every minute for thirty minutes.

Needle to left of zero.	*Needle to right of zero, (current reversed).*
28° 55′	28° 58′
28 55	28 58
28 55	28 58
28 55	28 58
28 55	28 57
28 54	28 57
28 54	28 57

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Needle to left of zero.	*Needle to right of zero, (current reversed).*
28 54	28 56
28 54	28 56
28 53	28 56
28 53	28 56
28 53	28 56
28 53	28 56
28 53	28 56

These observations show that the drop in current for half an hour was 2′ on left side and 2′ on right side or 4′ total. As 2′.5 correspond to about 1 milliampère for deflections of about 29 degrees, it will be seen that the drop of potential is very slight. The total resistance in the circuit outside the Bunsen cell, including galvanometer, resistance box and connections was about 12.6 ohms.

DECREASE OF CURRENT DURING A RUN.

Bearing this undoubted constancy of the potential of the cell in mind, an interesting phenomenon was observed when, in place of the metallic circuit, the electrolytic cell was used. This cell consisted, as heretofore mentioned, of a copper spiral anode and a copper cathode (composed of a platinum plate with a thick deposit of copper completely covering its surface), immersed in copper sulphate. The area of the plate cathode was 7 square inches, counting both sides. The area of anodes used was about 25 per cent. larger.

It was found that the current increased slightly during the first two or three minutes of a run using the electrolytic cell, and then fell off rapidly, the average deflection at the end of a half hour run being 26′ 5″ smaller than at the beginning. Subtracting from this the 4′ diminution of current due to the drop of potential of the cell as above quoted, it is seen that there is a diminution of the current corresponding to 22′ 5″, or about 8.8 milli-ampères in a half hour.

Following is appended the recorded observations of a typical

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run, the deflections given being the mean in five minutes of readings taken each minute:

Left side of zero.	*Right side of zero.*
28° 43′ 08″	28° 36′ 22″
28° 27′ 37″	28° 25′ 22″
28° 13′ 52″	28° 16′ 53″

This deflection corresponds to a current of about 0.183 ampères. The curve (Fig. 1) is plotted from the entire set of observations. The upper curve shows the drop in battery potential.

It will be noticed that after each reversal of the current through the galvanometer, there was a decided drop in the current, this drop becoming less and less as the experiment proceeded. The reversals were made at the end of each five minutes. Latterly, it was decided to reverse but once during the experiment, *i. e.*, at the end of the first fifteen minutes of the run. The deflection was much more constant in this case, but still showed the general tendency to increase a little at first and then drop off with comparative rapidity as mentioned before.

A platinum cathode was tried, but the polarization was so great that it was difficult to obtain accurate readings, the current fluctuating too much to allow a satisfactory observation of the galvanometer needle as is shown in the following table of ammeter readings.

AMMETER READINGS.

Zero reading = 0.

Time.			*Current.*
Hrs.	**Min.**	**Sec.**	**Milli-ampères.**
1	55	00	1800
		15	1820
		30	1825
		45	1830
	56	00	1840
		30	1870
	57	00	1880
	58	00	1900
	59	00	1910
2	00	00	1919

AVERAGE 185.85.

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Time.			*Current.*
Hrs.	Min.	Sec.	Milli-ampères.
	01	00	1910
	02	00	1910
	03	00	1910
	04	00	1910
	05	00	1905
		AVERAGE 190.9	
	06	00	1905
	07	00	1905
	08	00	1905
	09	00	1905
	10	00	1905
		AVERAGE 190.5	
	11	00	1905
	12	00	1900
	13	00	1900
	14	00	1900
	15	00	1900
		AVERAGE 190.1	

SOLUBILITY OF DEPOSIT IN ELECTROLYTE.

Another phenomenon observed was the solubility of the copper deposited on the cathode.

It was found that during the ten seconds while the cathode was being suspended in the electrolyte and before the current could be switched on, 0.2 mg. of the deposit was dissolved. This fact was determined as follows: The cathode, after having been deposited upon, was washed and dried, in the manner described, and weighed. It was then dipped in the same solution of copper sulphate which was used as the electrolyte. At the end of ten seconds the cathode was taken out, washed and dried as before, and when weighed was found to have lost 0.2 mg.

But it was found that this decrease in weight grew smaller with the number of immersions, losing in the fourth immersion but 0.2 mg., in *one minute*. This is clearly shown in the following table:

Cathode immersed in $CuSO_4$ (water 1000 cc., $CuSO_4$ 100g., H_2SO_4 1.5cc.)

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12.30 P. M. First trial—Weight of cathode before immersion 17.2365
After 10 sec. immersion 17.2363
Loss = .0002

1.30 P. M. Second trial—Weight of cathode before immersion 17.23630
After 10 sec. immersion 17.23615
Loss = .00015

2 P. M. Third trial—Weight of cathode before immersion 17.23615
After 30 sec. immersion 17.23595
Loss = .00020

2.30 P. M. Fourth trial—Weight of cathode before immersion 17.23595
After 1 min. immersion 17.23575
Loss = .00020

It will be seen from the time given when the experiments were performed that thirty minutes elapsed in drying the cathode between each of the trials except the first, when an hour elapsed.

A spiral copper wire cathode which had been deposited upon was washed, dried and weighed, and was left in the drier for three days. Upon removal from the drier it was found to weigh precisely the same. It was then immersed for ten seconds in the solution of $CuSO_4$ used as the electrolyte in these experiments, taken out and reweighed with the following results:

	Grams.
Weight of cathode before immersion.....	19.31445
" " after 10 sec. immersion.....	19.31425
Loss =	0.0002

This cathode was then immersed for ten seconds in a solution of one part H_2SO_4, eight parts water, with the following result:

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	Grams.
Weight of cathode before immersion in H_2SO_4	19.31425
" " after 10 sec. immersion in H_2SO_4	19.31425
Loss =	0.0000

There was no trace of oxidation visible on the cathode at any time during the weighing. Indeed, cathodes have been left in the drier (as above) seventy-two hours and the loss in ten seconds found to be the same, *i. e.*, 0.2 mg., showing that there had been no appreciable oxidation which was afterwards dissolved off by the copper sulphate. Also, when cathodes were dried and weighed and allowed to stand in the drier for two or three days, there was found to be no increase in weight.

It would appear that the surface of the fresh deposit is soluble to a marked extent in the electrolyte and that when, after this surface has been dissolved off, the cathode is of normal solubility in an acidulated solution of $CuSO_4$.

In calculating the current from the deposit of copper, this 0.2 mg. was always reckoned in the weighings.

It will be seen from the data given, that in accurate work with the copper voltameter it is necessary to allow in the weighing for the portion of the deposit which is dissolved off by the electrolyte before the current can be switched through the solution. This allowance must, of course, be determined experimentally for each particular case, as it appears to depend upon the size of the cathode.

Also, on account of the remarkable increase of polarization during the short time of open circuit necessary to reverse the current through the galvanometer, it is advisable to reverse but once during a run. Referring to Figs. 1 and 2, it will be seen that after each reversal of the current the rate of increase of polarization is large, but falls off with time until the next reversal when there is a large increase of polarization followed by a diminishing rate of increase of polarization, and so on. The breaks in the curves show the points where the current was interrupted to reverse it through the galvanometer.

In nearly all the runs a diminution of polarization was manifested during the first two or three minutes of the run as shown in Fig. 1. Some few runs did not show this as will be seen in

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Fig. 2, but in these cases the increase of polarization was very slight at first and then grew rapidly, falling off again towards the end of the run.

Annisquam, Mass., 1903.

DISCUSSION.

MR. CARL HERING: The copper voltameter, it seems to me, is not an instrument which could be used to make measurements to the fourth decimal place. I thought that was generally known. The very observations which the authors have made show that to use a copper voltameter for such accurate measurements is not justified. Is the electrochemical equivalent of copper known to such an accuracy as the fourth decimal place? Then the local dissolving of the copper which the authors say must be allowed for, it seems to me, will depend on the amount of acid, the duration of the test and the size of the plate. Also that this correction factor, if applied at all, would involve other quantities which are not accurately known. Again, it seems to me, that it is somewhat inconsistent to measure the earth's magnetism to such accuracy, because it varies, not only during the day but every minute, almost every second; so that the best that could be gotten would be its mean value for the half hour during which it was measured.

MR. BARRY MACNUTT: I would reply to Mr. Hering by saying that the solubility of the copper certainly does depend upon the sizes of the plate and upon the oxidation. In the experiments that we performed, however, there was no oxidation. We very carefully guarded against any oxidation as stated. I would also state, that on account of the close correspondence of our results, it would seem that we have eliminated, to such an extent, the errors that were due to the phenomena noted, that the results are believed to be accurate to the fourth decimal place. The observations were taken usually once a day, sometimes thrice a day, and, of course, we found variations in the earth's field during those periods.

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DR. GUTHE: Wouldn't those breaks in the curve indicate an increase in the polarization?

MR. MACNUTT: Yes, an increase of polarization.

DR. GUTHE: While the circuit is open?

MR. MACNUTT: While the circuit is open; which seems, of course, an anomaly; but those gaps were there in every curve and we made over 200 observations, all of which showed the same phenomena. The curves shown are, of course, current-time curves, and not polarization curves.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904. President Richards in the Chair.

ELECTROLYTIC IRON.

By Prof. C. F. Burgess and Mr. Carl Hambuechen.

A great deal of attention has been devoted of late to the application of electrical energy to the metallurgy of iron, and some of the results attained seem to point to developments of industrial importance. Most of the attempts to apply electrical energy have been through its transformation into heat for use in various smelting and reduction processes. That the electrolytic, as well as the electrothermal effect might be utilized industrially does not seem to have been considered seriously, as it has been commonly held that the difficulties inherent in the deposition of iron are such as to preclude its playing an important part in the industrial electrometallurgy of this element.

It has, however, been shown, as a result of recent experimental work carried on in the Laboratory of Applied Electrochemistry of the University of Wisconsin, that electrolytic iron can be produced in such quantities and at such cost as to make it a material of commercial as well as of scientific importance, should sufficient demand for it arise.

A survey of available literature on the subject of electrolytic iron leads naturally to the assumption that its deposition is difficult to accomplish, and that there are few solutions from which it can be deposited. Moreover, it has been held that a satisfactory quality of deposit can be attained only by the use of very low current densities and an exceedingly slow rate of deposition. Practically the only uses to which electrolytic iron has been put are in the so-called "steel facing" of dies and electrotypes, and as a material for investigating the properties of the pure metal.

The hardness of electrolytic iron, which makes it especially suited to the facing of electrotypes, is due to the occluded hydrogen, which is practically the only impurity present. In fact, the very term "electrolytic iron" is commonly assumed to be synony-

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mous with "pure iron." In just what manner the hydrogen is held by the metal is a matter of doubt, it being claimed by some that it is simply condensed, and by others that it forms a definite hydride. Such iron may contain this gas in quantities equal to several hundred times the volume of the metal, and it can be almost entirely freed from it by heating. Certain investigators have found that electrolytic iron contains carbon in appreciable quantities, while others have found that carbon is absent.

Dr. John A. Mathews (Alloy Steels, Mineral Industry for 1902) states that "pure iron may properly be classed among the 'rare metals'; thousands of tons of iron alloyed with impurities from a fraction of (one) per cent. upward are produced annually, but not a pound of iron in its pure elemental condition has ever been made under ordinary smelting conditions. By 'pure' we mean in a condition comparable with that in which the precious metals are produced, or as pure as the best electrolytic copper and nickel. . . . Just as pure iron is a chemical curiosity, so also is an alloy containing only iron and carbon. In practice at least four other solid elements occur fortuitously in all steels, viz., manganese, silicon, sulphur and phosphorous."

Something over two years ago the authors of this paper undertook an experimental investigation of the conditions suitable for electrolytically depositing iron, and this work has proceeded almost without interruption since that time. The primary object of the investigation was to produce, if possible, pure iron in such quantities and at such cost as to make it an available material for further inquiry into its properties. Since our attention has been confined almost exclusively to this phase of the problem, the observations which have been made as to the physical and chemical properties of the product are by no means exhaustive, and, indeed, are considered only as preliminary to a more extensive research which it is hoped to take up in the future.

The preliminary work consisted in testing the various electrolyte materials which had been suggested previously, and from these the most promising were selected as the basis for further trials. It is needless to record here the many hundreds of tests which were made, for most of them were unsuccessful; nor is it necessary to recite the difficulties encountered. The investigation was necessarily a slow one, since many of the trials required days and even

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weeks of operation before conclusions could be drawn as to their success. A large number of iron salts were used, and the effects of variations of density of solutions, current densities, temperature, agitation of electrolyte and various other factors were noted. As a result of such observation ferrous sulphate, with a certain percentage of ammonium sulphate, was chosen as affording the most satisfactory results, and the process as it is now being operated on a small experimental scale may be briefly described as follows: The electrolyte consists of ferrous and ammonium sulphates; the current density at the cathode is 6 to 10 ampères per square foot of cathode surface, and at the anode slightly less; the electromotive force for each cell is slightly under one volt; the temperature of electrolyte is about 30° C.; the anodes consist of ordinary grades of wrought iron and steel; the starting sheets for the cathodes are of thin sheet iron, previously cleaned of rust and scale.

One of the most serious difficulties encountered was in obtaining a thick deposit of iron. While it was proved that there is a considerable range of conditions under which iron can be deposited uniformly and densely for a few hours, or perhaps for a few days, it was almost always found that the surface would become so rough or pitted, or that such a rapid treeing would take place, or that the deposit would curl up to such a degree that it was necessary to discontinue the experiment and start a new one under different conditions. But improvements have been gradually effected, until at the present time it is possible to continue the run four weeks without replacing the cathodes. At the end of such time the cathode reaches an average thickness of about three-quarters of an inch, and the surface is so rough and nodular that it is not considered advisable to carry the deposition further.

The current efficiency of deposition is very closely 100 per cent.; that is, there is a deposition of about 1 gram per ampère hour. The electromotive force, being one volt, gives about 2.2 pounds of iron per kilowatt hour. Since all the factors which go to make up the cost of large-scale production cannot be accurately determined from a small-scale experiment, it is impossible to state, from our investigations, what would be the cost of working on an industrial scale. For the past six months three tanks have been maintained in almost continuous operation, these tanks having the dimensions of 8 inches wide by 13 inches long and 15 inches deep,

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and containing two anodes and one cathode. The finished cathodes from these tanks weigh about 20 pounds, and constitute, perhaps, the largest pieces of electrolytic iron which have, up to the present time, been produced. The total amount of the material which has been produced from all of our experiments is about a half ton.

A run of two months' duration was made to determine the extent of the deterioration of the electrolyte, resulting in the conclusion that the solution can be kept in good working condition with little trouble or expense. It would appear, therefore, that the cost of refining, aside from fixed charges on plant, and with power at $30 per kilowatt year, would be under ½ cent per pound of iron, thus placing it not greatly in excess of the cost of refining copper.

Even with these figures realized, whether or not electrolytic iron can be profitably produced depends upon the uses which can be made of the refined metal. These in turn depend upon its properties, the most striking of which is its purity. Although our work was directed toward the production of electrolytic iron in a dense and massive condition rather than in a high degree of purity, analyses which have been made show the purity to be in excess of 99.9 per cent. Not a trace of carbon was detected, and silicon, manganese and other impurities commonly found in iron appear to be absent. The only impurity which has been detected is hydrogen, which is present in appreciable quantities in the metal as taken from the electrolytic tanks. This gaseous element, in its physical or chemical combination with iron, influences, in a most striking manner, the physical properties of the metal. The hydrogen can be driven off almost completely, if not entirely, by heating to a white heat, the evolution commencing at a temperature below 100° C. and becoming rapid at a temperature below a red heat. Electrolytic iron heated in a Thomson welder, or even in a Bunsen burner, has been observed to give off hydrogen so rapidly that it ignites and continues to burn after removing the source of heat, presenting an appearance similar to that which would be produced by dipping the iron in alcohol and igniting it. The metal containing the hydrogen is so hard that it can be filed or sawed only with difficulty, and is so brittle that it is readily shattered by a sharp blow from a hammer. After the expulsion of the gas it becomes

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softer, and after having been raised to a welding temperature, it assumes properties of malleability and toughness similar to those of Swedish iron.

The iron, when heated in a forge fire, can be readily welded and forged into any desired shape, and various test samples were made in this way. During such working, however, impurities are introduced, analyses invariably showing the presence of a very small percentage of carbon. The cathodes, ¾ inch in thickness, have a surface so rough that they cannot be rolled satisfactorily into sheets, though it is possible that improvements can yet be made in this respect which will enable smooth surfaces to be obtained. The deposit adheres so loosely to the starting sheets that it can be removed readily.

A considerable amount of work has been expended in the attempt to melt electrolytic iron without at the same time introducing impurities. The difficulties that lie in the way of doing this, however, are great, on account of the high temperatures necessary, and the affinity which the iron at such temperature has for many of the elements. The melting temperature of the pure iron seems to lie closely to that of platinum, though actual values have not as yet been determined, from lack of suitable measuring instruments. Various forms of electric furnaces have been constructed for this purpose, a furnace of the inductor type appearing to be the most suitable for preventing the introduction of carbon. Results which have been somewhat satisfactory have been obtained by heating a molten electrolyte between graphite electrodes to a suitable temperature and introducing the metal into such molten bath. The metal thus produced is tough and malleable, while it also has a fracture of coarse crystalline nature. The affinity which the iron has for carbon is shown by the fact that it can be readily melted in a graphite crucible, while a silica crucible heated to a considerably higher degree melts before the iron in it begins to flow. The absorption of the carbon in the former case produces a fusible alloy of iron.

Experiments have shown that the hysteresis, permeability and electric resistance of electrolytic iron are greatly influenced by the amount of hydrogen in it. An iron ring was deposited in such form that a hysteresis and permeability loop could be determined by the Ewing method. It was found that by heating in boiling

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water the hysteresis was lowered several hundred per cent. By further heating in an oil bath to 200 degrees the value was decreased still further, but to a smaller extent than in the first heating; and upon attempting to heat it to 500 degrees the ring broke, and the experiment was therefore interrupted. Certain samples of forged iron have shown permeability values equaling, or even exceeding, those of the highest permeability standard samples of Swedish iron. Other samples, prepared under apparently identical conditions, showed much poorer results, so that it is impossible as yet to draw definite conclusions as to the magnetic properties of electrolytic iron.

It having been shown that it is possible for electrolytic iron to be produced at a small cost, the question naturally arises as to what uses there may be for it. The first suggestion which naturally presents itself is that, on account of its purity, it would serve as a basis for investigating the properties of iron and its alloys. Investigations having for their object the determination of the influence of various elements alloyed with iron, as regards its electrical properties, have been unsatisfactory on account of the presence of other impurities, which modify or mask the effect of the element which it is desired to study. Starting with the pure iron, therefore, alloys of a pre-determined and definite composition can be produced, thus making such investigations of greater simplicity. Unless the difficulties encountered in the working of electrolytic iron, on account of its roughness, offer too serious an objection, it should compete favorably with the purer grades of commercial iron, which are used for various purposes and which sell for 3 cents and upwards per pound.

Electrolytic iron naturally offers the means of manufacturing chemically pure compounds and for standardizing solutions in the analytical chemical laboratory. The electrolytic iron, in addition to its purity, has an advantage for the purpose just mentioned of rapidly dissolving in an acid solution. A test which was made to determine the rate at which electrolytic iron and iron wire sold as chemically pure for standardizing purposes dissolves, showed a ratio of one to twelve in favor of the former. By reason of the brittleness imparted by the occluded hydrogen, it can be readily broken up into grains of a desired size and even reduced to a fine powder.

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Although the investigations referred to in this paper have covered a considerable length of time, the work which has been done should perhaps be considered only as preliminary to a more extended investigation which it is hoped may be taken up in the future. Summing up the work thus far done shows that it is possible to obtain electrolytic iron in large quantities and at a reasonable cost, and that therefore iron should be added to the list of metals to which the process of electrolytic refining can be applied satisfactorily. It has been demonstrated also that such iron possesses a high degree of purity, though just how closely it approaches absolute purity can be shown only by spectroscopic analyses or by other methods which are more accurate than those which have been available.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

MR. W. MCA. JOHNSON: Some two years ago I made rather small-scale experiments on the electro-deposition of iron, and came to results similar to those of Professor Burgess. I found that the best electrolyte was a ferrous ammonium salt, and that it was advisable to add a small quantity of some organic acid which was not dissociated to any extent. The organic acid acts, as it were, as a reservoir and thus keeps the hydrogen ions at a fairly constant value. The chief trouble which I found was the fact that the ferric salts would become hydrolyzed and give the brown basic salts of unknown composition. I believe it is the usual custom when you have any trouble with a solution, to say that it is due to basic salts. I would suggest to Professor Burgess, if he cares to melt iron without contamination, to use as crucibles large Acheson round bars, hollowed out and brasqued with pure Al_2O_3, mixed up with water-glass of a specific gravity of 1.10.

One of the things that appealed to me in this paper was the fairly large scale on which the operations were conducted. I have done considerable experimental work in the last three years, and

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the thing which impresses itself on me is the great advantage of working, as soon as possible, with large quantities, say 50 to 100 pounds.

MR. CARL HERING: I was very much interested in the paper of Professor Burgess, and also in the remark that he made in the beginning—that there seems to be but little hope that iron could ever be reduced from its ores commercially by electric processes. I have myself made calculations concerning this matter as far as it concerns the wet electrolytic process, and have come to practically the same conclusion. One of the chief reasons why such a wet process would probably never be of any great commercial value, is that in the first place the quantity of tanks which would be required for depositing as many tons of iron as are now produced by some of the large furnaces, and at the same rate, would cover acres of ground. This alone would make it impracticable. Another reason is that the energy required would be very great, because in the blast furnace the energy of the coal combining with the oxygen of the iron is added to the heat of the furnace, while in the electrolytic reduction the oxygen would be given off as a gas, which means that an enormous amount of energy would have to be supplied in the wet process for the reduction of iron. If it would be possible to use some cheap material in the wet process which will combine with the oxygen, thus giving off energy, so that this great amount of energy would not have to be supplied from the outside, there might be a possibility for the success of the wet process for the reduction of iron from its ores; but such materials do not seem to exist.

MR. JOHNSON: I would ask Mr. Hering what kind of a solution was to be used in the wet process of reducing iron from its ores.

MR. HERING: The investigation did not go as far as that. It was simply a preliminary calculation to see whether there were any prospects at all, and whether it was worth while looking for any solution.

W. H. BROWN, JR.: What was the anode material in this process?

VICE-PRESIDENT CARHART: The paper stated iron.

MR. HERING: My remarks had reference to the reduction of iron ore; Professor Burgess' paper had reference to the refining

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of iron that had been reduced in the blast furnace. I would like to ask Professor Burgess what the reasons are that cast iron cannot be used. I notice he now says he used wrought iron or steel, and a year ago when I talked with him about this he said that there was some difficulty in connection with cast iron. It seems to me his process would be much more valuable if he could use a very cheap, low-grade cast iron, and it would therefore be interesting if in his reply he would state what the difficulties are with the low-grade cast-iron anodes.

MR. JOHNSON: I think I can give some sort of an answer to that. The point taken by Mr. Hering is a good one. Of course the cheaper the anode, the cheaper the process; but with the cast iron the effect of the alloys of iron, carbides and silicides, which do not conduct as well, and also have a lower potential than the pure iron in the anode, would be to make a large amount of scrap, which will all have to undergo a second treatment, and the slimes and scrap would fill up the bottom of the tank so fast that the plates would be short-circuited in three or four days.

MR. REED: It seems to me that the large amount of carbon and other impurities in cast iron as compared with that in the wrought iron and steel will be sufficient to make a very great increase in the difficulties of keeping the solution in working condition. It seems to me that would be a sufficient reason. It may be true, as Mr. Johnson has suggested, that cast iron would disintegrate and fall to the bottom, although that difficulty might be overcome by allowing the anodes to occupy a position in the bottom of the cell on a plate of graphite. The iron could then be used as an anode, even in a granular state.

MR. JOHNSON: Iron has such a very high electrolytic potential that there are few metals which could be alloyed with it which will not go into solution, provided the potential is kept at a comparatively low value at the anode. Zinc or aluminum never could come into the question. About as good an answer as I can give Mr. Reed is, "try it and see;" he will find that almost nothing but iron goes into solution.

PRESIDENT RICHARDS: Undoubtedly one of the chief difficulties of using a material like cast iron, which has only from 92 to 93 per cent. of iron in it, will be the same difficulties which are met in refining very impure copper; that the anode falls to pieces and

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the amount of anode scrap which is made and has to be remelted is very large and increases in a much greater proportion than the amount of impurities does. In using a comparatively pure material like wrought iron, or a nearly-refined copper, with over 99 per cent. metal, the anode wears away until it is almost as thin as a sheet of paper, and the amount of scrap is very much reduced; moreover, the annoyance caused by the falling of pieces of the anode itself from irregular corrosion, and its changing shape, are obviated by using the purer metal.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904, President Richards in the Chair.

THERMO-ELECTRIC DETERMINATIONS OF THE REDUCTION TEMPERATURE OF ZINC OXIDE.

By Woolsey McA. Johnson.

It is axiomatic to say that any determination which will give definitely any of the physical constants of a chemical reaction will be beneficial in working that reaction on a large metallurgical scale. In the reduction of zinc oxide by solid carbon, a reaction which absorbs considerable heat, a certain thermochemical potential must be reached before any chemical change takes place. According to the Gibbs-Helmholz equation in an endothermic reaction the free energy determines the velocity of reaction.

Before this point is reached the chemical potential of the reverse reaction is greater than that of the reduction. The difference of potential is a function of the difference of temperature between the "reaction temperature" and the temperature of the reacting bodies. If the function is a linear one and we have the reduction temperature at 1050° C., the reaction velocity when the reacting bodies are at 1100° C. will be five times as fast as the reaction velocity when the reacting bodies are 1060° C.

As has been pointed out by Professor Nernst, the rate of chemical change is equal to $\frac{\text{Chemical force}}{\text{Chemical resistance}}$, just as by Ohm's law ampères $= \frac{\text{Volts}}{\text{Ohms}}$. If we know the chemical force or chemical potential we have one means of determining the reaction velocity and consequently have a line on the rate at which zinc is reduced in a retort.

It is easy to say that to determine the reaction temperature all that is necessary is to heat up the components of the reaction with a pyrometer in them and observe the temperature at which the reaction starts, but as anyone who has had any experience in the

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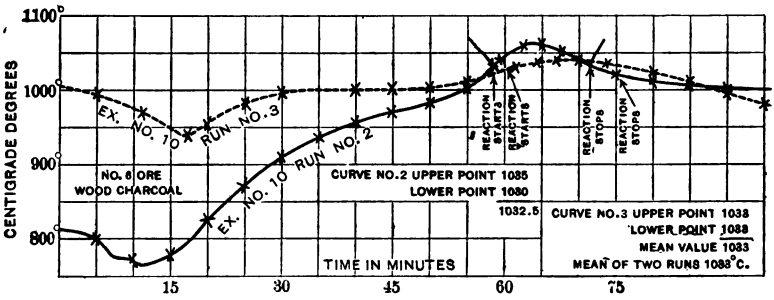
matter knows, it is found in practice that the lag of the reading in the pyrometer behind the reaction, and the temperature gradient of the charge give often very discordant results.

A practical cell to determine the reduction temperature of zinc oxide accurately and quickly should conform to the following conditions:

1. The cell should be made of a refractory material not reacting with the substance to be tested.

2. The cell should be tight that the products of the reaction may escape through one small hole so as to make a bright and sensitive flame.

3. The cell should conduct heat to the charge and to the pyrometer so easily that the pyrometer junction and the charge are always at nearly the same temperature.



After some experimenting with fire-clay and fire-clay mixed with graphite, the substance which we found to fill best these conditions was solid Acheson graphite bars such as are suitable for the electrolysis of zinc chloride. The round bars, it may be remarked, make almost a perfect crucible if machined out on a lathe.

The cell which we finally adopted is described as follows:

A four-inch round Acheson electrode is cut off in pieces four inches long. A two and one-half inch hole is drilled in this round bar on a lathe, its axis being the axis of the bar. A thread is cut in the top of the hole to receive the threaded cover, also made of graphite. In the lower part of the cell a three-fourths inch hole is drilled to receive the pyrometer, one-half inch of graphite being left between the charge and the pyrometer. All this work is done accurately by machine tools, for as is well known it is possible to machine Acheson graphite accurately.

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Just below the line of the charge a one-fourth or three-eighths inch hole is drilled. This hole is tapped to receive a threaded iron or graphite pipe which is used in case the indicator is carbon monoxide gas and not zinc. When the zinc flame is used as an indicator this pipe is not screwed into the hole.

The pyrometer we used was the usual platinum-iridium platinum couple with the galvanometer reading directly in degrees Centigrade. It was furnished by Eimer and Amend and had been certified by the German Reichsanstalt. We used a broken outside porcelain tube in preference to a new porcelain tube because the radiation by the graphite on the junction gives very quickly the temperature of the cell to the pyrometer junction.

The procedure in determining the reduction temperature is as follows: Equal parts of the material to be reduced are mixed with the reduction material filling the cavity to about one-half its height. A little of the coarse reducing material is sprinkled over the top. The cover is next screwed on and the cell put in the furnace. The furnace is a specially built experimental reverberatory furnace fired with natural gas and equipped with a heater for the air and with checkerwork to make a quick combustion. A ten inch graduated dial on the handle of the gas valve allows accurate adjustment of the flow of gas and a damper allows accurate adjustment of the flow of the air. By a proper regulation of the temperature and flow of air and flow of gas it is possible to have a radiant flame consisting of hot particles of carbon of almost any temperature from 900 to 1600° C. This radiant flame heats the cell without undue oxidation of the graphite. The degree of regulation can be seen in the curve of experiment 10 where in the second determination the temperature increased as a linear function of the time 30° in thirty minutes.

The pyrometer is next inserted into the cell and clamped to a wrought iron support outside the furnace. It is then connected to a permanent circuit leading to the galvanometer. The galvanometer is placed on a pier made of bricks laid in cement about six feet from the furnace. The door of the furnace is partially closed with a block of fire-brick.

The temperature is first raised quickly and a rough determination made of the temperature at which the snaky flame is given off. The cell is cooled down and the temperature at which the zinc

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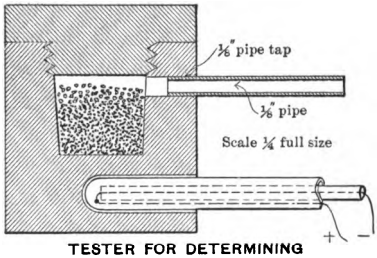
ceases to be given off is taken. The mean of these two values is then within 10 to 15 degrees of the true value. The last one is usually fairly close to the final value. Now the gas is turned on again and the temperature of the cell raised very slightly at the suspected temperature. While one observer reads the pyrometer and regulates the gas, the other watches the small hole in the cell for the zinc flame. When the reaction starts, the observer, reading the pyrometer, is notified and the point where the reaction starts is marked down on the curve which is plotted during the determination. The temperature of the cell is raised 5 or 10 degrees to insure that this is the real reaction and not a chance reaction, due to impurities in the mixture. If the reaction is the real reaction and not a "false reaction," the evolution of zinc and carbon monoxide increases rapidly with the temperature. The temperature is then



TESTER FOR DETERMINING REACTION TEMPERATURES.

lowered slightly and the point at which the reaction stops is noted down. Two or three determinations are made and the mean of the means taken as the true value. The means usually agree within 2 or 3 degrees with each other. If the values are not concordant the reason is to be found in an inhomogeneous charge.

Thus, in one experiment the preliminary value was found to be 1020° C. We accordingly raised on the first determination the temperature quite rapidly to 1020° C. and then slowly. The reaction started at 1035 degrees and stopped at 1030° C., giving as a mean 1032.5° C. On the second trial the reaction started at 1033° C. and stopped at 1033° C., giving a mean of 1033° C. and a mean of means also of 1033° C. We have made even closer determinations than these, but of course this would be due to chance, and the above is a bit better than the average.

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In no case was the barometric observation taken which, however, would not cause a variation of over two or three degrees. In Kansas, however, one might expect great variations of pressure and in the future the pressure will be determined. If the furnace had happened to be in the vortex of a cyclone, there might have been considerable effect on the readings, to say nothing of the effect on the observers.

A glance at the tables below brings out quite clearly what has been the somewhat indefinite opinion of zinc smelters from practical observation, namely, that the temperature of roasting effects the ease of reduction and that different reducing materials have different rates of reduction. It might be mentioned that similar results were found by the distinguished English iron master, Sir Lowthian Bell, some fifteen or twenty years ago, with the oxides of iron, if, to quote Ovid, "we may compare great things with small." Also in analytical and manufacturing chemistry the effect of heat on the dissolution of solids by acids is well known.

Our idea is that the reduction of zinc oxide is caused by the very slight vapor pressure of solid carbon and the slight dissociation pressure of zinc oxide, tending to break up the zinc oxide into zinc and free oxygen. It is easy to imagine the effect of heat in making a denser and more stable configuration of the atoms in the molecule on reducing these vapor pressures. I can even conceive how the change is an electrochemical one in its nature, and that the electrons play a very material role. At all events, after the forming of this hypothesis we were greatly strengthened in our faith in it by reading* that the French savant, Berthelot, in the "Académie des Sciences," had arrived at similar conclusions, only in a much more complete and developed form. These results and conceptions tend to show that the primary reduction of zinc oxide by carbon is not caused by carbon monoxide, although there is no doubt that carbon monoxide does tend to increase the rate of reduction after the primary reduction is once started. The above, however, is more an opinion gained by intuition from seeing many experiments on the reduction of zinc rather than any rigid deduction from the experiments.

In conclusion, I might state that the work was done under my direction in the metallurgical laboratory of the Lanyon Zinc Co.,

* Engineering Magazine, p. 597, Jan., 1904.

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by Mr. Walter Chapman, with my assistance during the preliminary experiments. I take pleasure in putting on record the very accurate and careful work which Mr. Chapman did after I put the matter in his hands. I also wish to express my thanks to Mr. F. E. Drake, president of the Lanyon Zinc Co., for allowing me to publish these results. It is done from a sense of enlightened self-interest, with the hope that the spirit of "do ut des" may extend the custom of publishing the scientific results of technical laboratories.

REACTION TEMPERATURES.

Material to be Reduced.	Reducing Material.	Corrected Mean of Means. Degrees Centigrade.
C. P. zinc oxide	1100° charcoal	1022
C. P. zinc oxide, calcined at 1300° C.	1100° charcoal	1025
C. P. zinc oxide	Soft coke	1029
C. P. zinc oxide, calcined at 1100° C.	Soft coke	1048
C. P. zinc oxide, calcined at 1300° C.	Soft coke	1061
C. P. zinc oxide	Graphite turnings	1084
Roasted Colorado ore	Soft coke	1029
Roasted Joplin ore	Soft coke	1073
Roasted Joplin ore	Very soft, 600° charcoal	1033
Roasted Joplin ore	1100° charcoal	1059
Roasted Colorado ore	1500° charcoal	1073
Joplin ore	1500° charcoal	1080
Joplin ore	Graphite turnings	1116
Colorado ore	Graphite turnings	1120
B. P. cadmium		756
C. P. cadmium oxide, made by wet method	600° charcoal	767
C. P. cadmium oxide, made by wet method	1100° coke	813
C. P. cadmium oxide, made by wet method	Graphite turnings	849
Zinc sulphide, from Joplin	Cast iron filings	1167

Same coke used in all experiments, made in forty-eight hours in bee hive ovens. It analyzed as follows:

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Eighty-seven per cent. fixed carbon; 1 per cent. volatile; 12 per cent. ash.

Joplin ore from bin, roasted at about 1050° C.

Colorado ore from bin, roasted at 900° to 950° C.

Charcoal was made by heating at definite temperatures Southern pine in a large covered crucible until volatile matter ceased evolving.

DISCUSSION.

MR. W. R. MOTT: I would like to ask one question, and that is as to the efficiency obtained in this work, and how it compares with the Brown electrical furnace, patented by Brown and Oesterle (November 3, 1903)?

MR. W. MCA. JOHNSON: The efficiency was very small, perhaps one millionth of a per cent. We use a few grammes only in the cell, which is but 4 inches high, and it is heated with a large stream of gas. It is simply a scientific determination made to determine the reduction temperature of zinc, which has never been done accurately before, and these are very accurate determinations.

MR. H. L. CABOT: I should like to ask Mr. Johnson if he has ever tried to reduce the oxide of zinc by the direct action of natural gas? That has nothing particularly bearing upon this; but still, it is of technical interest.

MR. JOHNSON: A great many experiments have been made in that line by other men, and I have made some myself, without any satisfactory results up to the present time. In those tables, you will notice, that I found the boiling point of cadmium lower than the value found by Berthelot and I also found the reduction temperatures of cadmium oxide (chemically pure) to be 200 degrees below that of zinc—somewhere around 800. On hearing the two papers by Professor Carhart and Dr. Wolff on Thursday, it struck me that by making a cell much larger than this by inserting a pyrometer and adding a condenser (also made of graphite), it would be easy to distil over pure cadmium, without a hundredth of a per cent. of zinc.

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PRESIDENT RICHARDS: The form of furnace Mr. Johnson has used is undoubtedly one which can be used by electrochemists for a number of different kinds of experimental work, and I think that of itself would be sufficient reason for bringing this before the Society. Especially for electrometallurgical work, and the investigation of the electrolysis of salts at high temperatures, or the passage of electric current through mixtures at high temperatures, a form of furnace of that sort with the thermo-couple inserted immediately below the working chamber would be of great advantage.

I was very much interested in the statement that Mr. Johnson makes, although he made it with some reservation—that carbon vapor was probably an active agent in starting the reduction of the zinc oxide, and he said that he had arrived at that more by intuition than by any real proof. About in the same manner (that is, by intuition), I have had an idea that the vapor of carbon probably plays a considerable part in the reduction of silica in a carborundum furnace. I have no proof of this, but it seems to explain some points which are apparently otherwise inexplicable, and I think that at the temperature of the carborundum furnace, for instance, the vapor tension of silicon and of carbon are considerable enough to play an important part in the reduction of some of the difficult reducible oxides which are present.

MR. JOHNSON: I might emphasize again what a fine material Acheson graphite is for making all sorts of cells for high-temperature experimental work. It can be machined down accurately, will stand pressure and is immune to changes, and some time when we have time we will make an apparatus machined accurately for determining the latent heat of vaporization of zinc, which has been calculated in two ways, but has never been determined. We also intend building an electric furnace for high temperatures, and we want to see if we cannot determine the reaction temperatures of magnesia, silica and alumina by this same method. Of course, in that case we would have to use as an indicator carbon monoxide gas, because I believe the reduction temperatures of those oxides are below their boiling points.

THE CHAIRMAN: Any further discussion?

MR. C. J. REED: It seems to me there is abundant evidence that carbon vapor does not exist at temperatures below 2,000

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degrees. We could not have any practical incandescent lamps with carbon filaments if it did, as they would blacken almost instantly so as to become opaque. The fact that we have carbon lamps burning at temperatures above 2,000 degrees for weeks without the slightest blackening, I think proves pretty conclusively that any carbon vapor that exists, even at the temperature of the lamp, must be too small to be considered at all, or measured in any way.

MR. JOHNSON: Of course, it goes without saying that the carbon vapor is very small, but nevertheless it does exist, as shown by the blackening of the lamps.

MR. CABOT: It seems to me that the phenomenon of a reaction between carbon and zinc oxide simply presupposes that one or the other is sufficiently molecularly active to approach the other. That two things come together does not mean necessarily that they both move; it means that one of them moves, or the sum total of the two motions is sufficient to bridge the space between them.

Mr. Johnson has instanced the appearance of a slight film of carbon in the interior of incandescent lamps as a proof that carbon was to a certain small degree volatilized by the heat of the incandescent lamp. It doesn't seem to me that that is proof positive that it is volatilized by the heat of the incandescent lamp alone. We have there a current, and that is not the condition of a simple heated furnace. It seems to me probable from what we know of electric furnaces that the small sublimation of carbon in incandescent lamps is conditioned by the current—plus the heat, perhaps—but at any rate that the heat without the current would not cause it. We know, for instance, that carborundum is made in an electric furnace by a very high temperature—I am not able to say at what temperature; if that temperature be raised much higher still, to a point sufficient to volatilize and vaporize the silicon, we thus obtain this very graphite which Mr. Johnson has used as the material for this furnace, which is left and is not volatilized at a temperature sufficient to vaporize silicon. Now it seems to me that in this furnace of his, his oxide of zinc is more likely to be active than the carbon.

MR. JOHNSON: In reply to that I will say that if you heat the reducing material you raise the reduction temperature, and if you heat the zinc oxide you raise the reduction temperature. There

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is almost a hundred degrees centigrade between the extremes. If you will look at the table, you will see that the zinc oxide, calcined at about 1,050 degrees, has a much higher reduction temperature with the same reducing agent than zinc oxide made by a wet method, and that also zinc oxide reduced by a soft charcoal (made at 600° C.), has a very much lower reduction temperature than zinc oxide reduced by Acheson graphite, which has been subjected to three or four thousand degrees centigrade. Thus, the effect of heat on either the reducing material or zinc oxide will raise materially the reduction temperature.

I might add that this change of the reducing activity of the carbon is more or less the basis of the "carbon-vapor" theory which I thought out and which I saw fully and beautifully developed by the Frenchman, M. Berthelot.

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EXHIBITION OF POROUS PLATE.

By S. S. Sadtler.

Mr. Sadtler: This is not an invention of mine but that of a young man of Philadelphia, who came to my office the other day and was talking about porous plates that he was making. It interested me very much, and I believe it would interest almost every one here for experimental work and for larger scale work. These plates were broken in arriving here, but they are made 9 x 6 inches, and they consist of a very thin plate 1-16 inch, supported by a grid of the same material pressed so as to be considerably thicker, maybe something over an ⅛ of an inch. He says he can make these about a foot and a half square, and might be able to make them larger. His patent consists of several claims—of the supporting portions and the grinding down of this surface so as to make it perfectly true. I will pass around some of these fragments, and if anybody is interested in getting plates for experimental work, I will direct them where to apply.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904, President Richards in the Chair.

AN INDEX TO ELECTROCHEMISTRY AND ITS APPLICATION.

By Adolph L. Voege.

When a piece of scientific experiment is undertaken at a university to-day, the advice is to devote two-thirds of your time to the literature of the topic. The detailed study of the works of our predecessors must obviously be done personally; but no one who has made the attempt will fail to appreciate the enormous difficulties that exist to-day in finding out what has been published the world over on any given topic. And yet let the student overlook one single reference, published, perhaps, in a foreign tongue and in an obscure journal, and he may suddenly awake to the desolating realization that his long months of study have been useless and that he has merely rediscovered a fact long since known. Perhaps the overlooked paper may contain suggestions which, if known in time, would have given a totally different trend to his work, so that he falls short of discovering vital features and finds that his labor has been almost useless; he may even find that another, better posted on what has already been done, has with far less pains come to valuable results, which would have been his, had he only learned in time of that earlier work. A manufacturer sees a by-product more or less wasted, when perhaps in some other land this same product is turned to good account. Who has such encyclopædic knowledge that he can advise him? Think of the inventors who are wasting their lives by not being able to know in time the partial solutions their problems have already received. Who can tell us how many unforeseen applications may be made of a process devised merely to meet one special need?

These are things that individual effort can never attain. Here organization is the salvation. Let us found a central agency where the work will be done once for all. Personal conviction and the advice of leaders in electrochemistry brought this need home

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to me some time ago and I have resolved to devote my life to the task, if I could only count on the support of the very persons who would be benefited by my work. It is evident that foreign work is least known in America, and during my stay in Germany, I set to work to gather all the information possible in the great libraries. Later, chance brought to my knowledge the fact that zoölogists had met similar needs by an organization such as I had planned and that the same was in successful operation in Zurich, Switzerland, under the name of Concilium Bibliographicum. It seemed at once to me that if a theoretical science such as zoölogy, could find advantage in such an institution, this must be still more the case for a science where great financial interests are involved, and I found, on studying the methods used in the Concilium, the best possible illustration of the time-saving that such a work will yield. Here I had been independently working on this question only to find the problems and methods already solved and to such perfection that I could take a new start from what had already been done.

No book index can possibly serve our purpose. In a growing science a book becomes out of date while it is going through the press. It cannot be corrected, it cannot be expanded. Alone the card system, in which each work as it appears is indexed on a separate card, will answer.

Let us suppose an institution established for our science similar to the Concilium, and let us see what it will do for us. In some center, an office is established which works through all the technical and scientific literature of the world. In electrochemical journals, as well as in such which an electrochemist would never consult, valuable observations are found and recorded. In advance, a list of all the topics in regard to which information may be asked is prepared, and the cards find their way to the appropriate heading, or headings—for one must consider all the applications and relations of a new fact. Let us assume that there is a heading to receive references on injuries to street mains by stray electric currents. I am confident that were the work now in existence, one would be astounded at the places in which valuable notes on this theme have been published. I am furthermore convinced that the references supplied by such an institution would be more complete than any individual effort could secure. The card index

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should be a printed index, so that a letter to the office calling for information on the topic mentioned, as an example, could be at once answered by sending that collection of cards. In this, the central bureau would serve as a bureau of information; but it is evident that for financial support it would depend largely upon libraries, institutions and, in a measure, industrial undertakings becoming subscribers to the whole bibliography or a considerable portion of it.

When the central office attempts to answer such a specific question as above cited, it is evident that the applicant has little interest to know by what technical method the references are picked out for him. But the purchaser of any considerable part of the index will want to know how to arrange his cards, so that he too can put his hand on any question that concerns him. This can be done, if a technical device can be found which will permit each subscriber to duplicate the arrangement of the cards found in the central office. We could not expect the receiver to learn our system by heart, so that when a new card comes he will know just where to place it. Instead, we should use symbols printed on the cards which show exactly where the card belongs without considering the text. The simplest symbols are Arabic numerals and the most convenient way of using them is to arrange them as decimals, so that in the symbol 621.3, 62 is a sub-division of 6, 621 of 62, and 621.3 of 621.* A little thought will show that such a system permits endless expansion. As to the selection of numbers, it seems wisest to keep in touch with the most widely used system of the day, namely, the so-called decimal classification of Melvil Dewey, librarian of the New York State Library at Albany. In view of the special character of our work, this system must, however, be considerably expanded. I am undertaking this with the aid of specialists and the whole will ultimately be published in a key or "Conspectus."

Without, however, in any sense neglecting the theoretical aspect, it is intended that the new bibliography should be *practical,* for the urgent uses of the practical man. For this reason patent literature will be exhaustively treated. For so young a science as ours, it ought to be eventually possible to run back the bibli-

* In the scheme, 6 means Applied Science; 62 Engineering; 621 Mechanical Engineering; and 621.3 Electrical Engineering.

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ography to the beginnings of the science; but *at the start* the current literature should receive first attention.

Of the enormous value of such an undertaking, there can certainly be no doubt; we have now to consider whether it is possible to carry it out. Here it will again be necessary to say a few words in regard to the Concilium Bibliographicum. This enterprise was rendered possible by the action of the zoölogical societies of the world and by private generosity. The founder, Dr. Herbert Haviland Field, made at the start considerable financial sacrifices for the work and devoted several years to it without receiving any compensation.

At present the finances of the Concilium are such that with strict economy the staff can be paid fair salaries, and the deficit is merely that covered by the annual subsidy of $1,500. The prospects are good for further improvement. Much of the expense of the Concilium consists in the maintenance of the general plant, including, as it does, a specially equipped printing office. Work done in connection with the Concilium would not only profit by nine years experience, but would also receive the equivalent of a considerable subsidy in being able to use in part the general plant. The founding of a section of electrochemistry, in connection with the Concilium, is in accordance with the general policy of the institution. Indeed, arrangements have been made for the advance of certain funds towards the first preliminaries of such a section. These circumstances seem to decide the location of the new bureau in Zurich; but there are other reasons for such a decision. Labor is much cheaper than in America, the library facilities are excellent and are being constantly improved. Moreover, when one considers the prime function of such a bibliography, viz., that of bringing to the notice of fellow-workers matter that would have been otherwise overlooked, it is evident that to aid Americans, the best possible location is the center of Europe. What work is liable to be overlooked in America? Surely not that published in *The American Chemical Journal, The Electrochemical Industry, The Electrical World.* No, the great need is completeness of reference to work being done in less accessible places—in some hidden corner of Germany, in Russia, perchance. In this, appears then the great value of such an American outpost as we have described—right in the very heart of Europe—in this little active country of Switzerland with its three national languages.

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The experience of the Concilium teaches us that such an undertaking ought to succeed. But all depends upon the support that members of the electrochemical fraternity can muster. I have, therefore, taken the liberty of making a direct personal appeal to the members of the society, and of asking them to return to me the post-card sent with this paper. It would also be very desirable if they would urge the matter on friends not members of the society, and above all would try to secure for us promises of probable subscriptions to the *whole* collection of cards on the part of libraries and industrial enterprises. Surely no library connected with a school of science can afford to be without this only means of keeping abreast with the times. We have prepared a provisional schedule of prices which, to our minds, represents the maximum. It is quite three times the rate the Concilium has introduced for its other branches. The latter low rates will be approximated, when the number of subscribers is sufficient.

In closing, I may be permitted to enumerate briefly, as examples, some of the topics that might be chosen for subscription:

Complete subject cards.
Complete author cards.
Cards geographically subdivided.
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Complete applied science cards.
The complete patent cards.
Patent cards of special countries.
Electrochemical theories and dissociation.
Mass action.
Polarization.
Electrolysis of mineral salts—pure or applied science cards.
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Primary cells.
Accumulators.
Electrometallurgy.
Electro-radiant energy.
Apparatus—experimental or industrial.
Plans and reports of plants.
Electro-therapeutics.
New books.

This paper has been prepared in collaboration with Dr. Field, director of the Concilium.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904, President Richards in the Chair.

OBSERVATIONS ON THE PREPARATION OF ELECTROLYTIC WHITE LEAD.

BY C. F. CARRIER, JR., A. C.

The original patents of Luckow[1] specified that a 1½ per cent. solution of a mixture of 90 parts $NaClO_3$ and 10 parts Na_2CO_3 should be electrolyzed between a hard-lead cathode and a soft-lead anode, CO_2 and water being added as required. It was shown, however, by Le Blanc and Bindschedler[2], and A. Isenburg[3], that true white lead could only be produced when the CO_2 is greatly diluted with air. The most satisfactory proportion was found to be 1 part CO_2 to about 20 parts of air. In this case, however, the absorption of the CO_2 by the electrolyte is by no means complete, and provision for re-use must be made, or great loss will ensue. The question now arose as to whether basic lead carbonate of the desired composition could be produced by some process differing essentially from that of Luckow.

The process of Richards and Roepper[4] was chosen as the subject of the experiments. This consists in electrolyzing a 5 per cent. solution of a mixture of 1 part Na_2SO_3 and 40 parts CH_3COONa with lead electrodes, a small quantity of some nitrate being added to aid the solution of the anode. With a current density of 100 to 200 amp. per m^2, the acetic acid anions are supposed to be decomposed at the anode, yielding CO_2 to precipitate the white lead, the necessary admixture of hydroxide being formed by action of the sulphite. According to the specifications, the following experiments were made:

Preliminary trials: The apparatus consisted of a 2½l. accumulator glass arranged, with one anode and two cathode plates. The

[1] D. R. P. 91,707 and 105,143.

[2] Zeitschr. f. Elektr. 8, p. 255 (1902).

[3] Zeitschr. f. Elektr. 9 p 275 (1903).

[4] U. S. P. 644,779.

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active anode surface was 500 cm^2. On the first trial a small quantity of white precipitate was formed, but at the same time spongy lead was falling in lumps from the cathode. A second attempt was equally unsuccessful. It was then attempted to overcome these difficulties, each run continuing from three to five hours, and a trial, according to Isenburg's modification of the Luckow method being carried out under similar conditions for comparison.

Experiment No. 1.—All conditions same as in preliminary trials except that a mixture of 5 parts air to 1 part CO_2 was passed through the electrolyte. The anode dissolved with 100 per cent. efficiency, but the yield was only 91.81 per cent. of the theoretical, the loss being largely due to spongy lead deposited on the cathode. The voltage rose from 2.4 to 2.8 in the first half hour. Product largely carbonate. (See tables below.) Anode badly pitted.

Experiment No. 2.—Solution 1½ per cent. of mixture of 80 parts $NaClO_3$ and 20 parts Na_2CO_3. Current density, 50 amp. per m^2., CO_2 of same dilution as in Experiment No. 1. The voltage ran from 2.8 to 3.10 in fifteen minutes. Solution efficiency of anode, 92.72 per cent.; yield, 92.71 per cent. The cathode was coated with a very thin layer of finely-divided lead from the action of sodium ions on the lead, for which reason copper cathodes were used in the next experiments. Product was more basic than No. 1, although still mostly carbonate.

Experiment No. 3.—Solution 5 per cent. of CH_3COONa with no Na_2SO_3. The proportion of air to CO_2 was increased to 20:1. Other conditions same as in No. 1. In spite of the rapid current of dilute CO_2, lead was rapidly depositing on the copper cathodes and the voltage rose from 1.6 to 2.0 in five minutes. To stop the deposition of lead a small quantity of Na_2CO_3 was added. Solution efficiency of anode was again 100 per cent. and the yield increased to 96.75 per cent., but it proved to be too basic.

Experiment No. 4.—Solution 1½ per cent. of mixture of 90 parts $NaClO_3$ and 10 parts Na_2CO_3. Proportion of air to CO_2 20:1 and other conditions as in No. 2. Voltage rose from 2.1 to 2.8 in fifty minutes. Solution efficiency of anode, 99.67 per cent.; yield, 98.4 per cent. of composition similar to No. 3. In this, as in all cases, some lead was deposited on the cathode.

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TABLE OF COMPOSITIONS OF BASIC LEAD CARBONATES.

	$PbCO_3$.	= 77.53 % Pb
	$7PbCO_3$. $Pb(OH)_2$	= 78.48 % Pb
	$5PbCO_3$. $Pb(OH)_2$	= 78.81 % Pb
*	$3PbCO_3$. $Pb(OH)_2$	= 79.46 % Pb
	$2PbCO_3$. $Pb(OH)_2$	= 80.13 % Pb
	$3PbCO_3.2Pb(OH)_2$	= 80.67 % Pb
	$4PbCO_3.2Pb(OH)_2$	= 80.90 % Pb
	$Pb(OH)_2$	= 85.89 % Pb

TABLE OF RESULTS.

No.	Percentage of Pb I	Percentage of Pb II	Solution Efficiency of Anode.	Yield.
1	78.28	78.18	100.00 %	91.81 %
2	78.89	78.74	97.72 %	97.71 %
3	80.74	80.73	100.00 %	96.75 %
4	80.84	80.81	99.67 %	98.43 %

The analyses were made electrolytically as PbO_2 and were run in duplicate.

The scope of this investigation is not sufficient to justify the drawing of positive conclusions, but a few observations on the results may assist in throwing light on the subject of electrolytic white lead production.

1. As might be expected, the use of copper cathodes reduces the voltage between the cell terminals.

2. With a current density of 100 amp. or more per m^2, the anode dissolves irregularly, "pitting" badly.

3. With a solution containing enough hydroxide to precipitate white lead, spongy lead is deposited on the cathode, even in Experiment Nos. 1 and 2, where the product was largely carbonate.

4. To prevent a large deposit of lead on the cathode, it would seem necessary to have a permanent store of CO_3 ions in the solution, thus making Na_2CO_3 or other soluble carbonate an essential constituent of the electrolyte.

5. The solution effect of nitrates on lead, when added to the acetate solution, seems to have a higher efficiency than chlorates alone.

* According to Thorpe's "Dictionary of Applied Chemistry," good white lead must lie between $3PbCO_3.Pb(OH)_2$ and $2PbCO_3.Pb(OH)_2$.

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6. The tendency of lead to deposit on the cathode is less with the more dilute solution.

7. To procure basic carbonate of the proper composition requires a fineness of regulation of CO_2 dilution beyond the command of the author's apparatus.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904, President Richards in the Chair.

ELECTRIC SMELTING EXPERIMENTS FOR THE MANUFACTURE OF FERRO-NICKEL FROM PYRRHOTITE.

By Ernst A. Sjöstedt.

It having been my good fortune, a few years ago, to be entrusted with the interesting task of carrying out a series of smelting experiments for the manufacture of ferro-nickel metal from poorly-roasted pyrrhotite, it has occurred to me that an abridged description of the same may, possibly, be of interest to this society, and that, perchance, they may deserve a place among the records of pioneer work in this line, although not having resulted in the establishment of a plant on a commercial scale, as at first expected.

The problem presented for solution consisted in the utilization, to the best advantage, of the nickeliferous pyrrhotite of the Sudbury district (a monosulphide of iron or "magnetic pyrite," with 2 to 3 per cent. Ni and 1 to 2 per cent. Cu), with special reference to the saving of the sulphur and iron, as well as the nickel and copper contained in the ore—the common practice being to allow the sulphur to escape in the process of heap roasting, and the iron to be fluxed off and wasted in the slag. After having made some attempts at magnetically separating the nickel from the copper ore and the barren gangue, and this not proving satisfactory, it was decided to hand-sort the ore at the rock house, using the grade higher in copper and gangue for the ordinary matte smelting, and the grade low in copper and gangue but high in sulphur and nickel for the ferro-nickel industry. This latter grade of ore usually averages about 3 per cent. of nickel, 0.5 per cent. of copper, 28 per cent. of sulphur, 50 per cent. of iron and 0.01 per cent. of phosphorus.

Our first idea was to subject this ore to a thorough desulphurizing treatment, so as to convert it into an oxide of iron and nickel low in sulphur (copper and phosphorus), *i. e.*, into an ore suitable for the manufacture of a ferro-nickel pig by the blast-furnace process; this pig metal to be further treated by the open hearth or Bessemer process for the manufacture of a ferro-nickel

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steel. But the first roasting experiments not proving very satisfactory, resulting in a product still carrying 7 to 8 per cent. sulphur, and, arguing from the fact that everything in the blast furnace practice points to an elimination of sulphur by means of a basic charge and a high furnace temperature, it was reasoned that, in order to yield a satisfactory product, this ore with such high sulphur contents, would require a large excess of basic admixture, which, however, would result in a slag too refractory for being kept fluid by the blast furnace heat, and thus calling for a greater source of heat—such, for instance, as obtainable by the electric energy. A large electric plant being at our disposition, it was therefore decided to attempt the reduction and smelting of this ore in an electric furnace.

Our first electric smelting experiments were made in a plumbago crucible, 8 inches high and 4 inches inside diameter, using only ½-inch carbon pencil, but, subsequently, 2, 4 and 6 carbons were bunched together. The crucible was placed on strips of copper, resting on copper wires, which were connected with the electrodes. The power used was 75 amp. from a 100 volt dynamo. Different proportions of finely-crushed ore, lime and coke were used, and the resulting metal beads analyzed, thereby clearly establishing the following facts:

1. Raw pyrrhotite is only partially and with difficulty converted into a metal—no good arc being obtained in these experiments, the indicator oscillating from 0 to 150 amp., proving the mixture to be too good a conductor (the raw ore possibly being too magnetic?)

2. A partially-roasted pyrrhotite, in a mixture of lime and coke or charcoal will be reduced to a metal—the carbon in the coke combining with the oxygen of the roasted ore, and the sulphur partly volatilizing or oxidizing, and partly combining with the lime, which also combines with the silicious matter in the ore and the coke, forming slag, and with part of the carbon to calcium carbide (the presence of which was always noticeable).

3. The larger the lime charge, the smaller will be the amount of sulphur in the metal produced. For instance, an ore containing 7 per cent. of sulphur produced, with a charge of 20 per cent. lime, a metal of 1.6 per cent. sulphur contents; with a charge of 50 per cent. lime, a metal of 1.5 per cent. sulphur contents; with

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a charge of 150 per cent. lime, a metal of 0.06 per cent. sulphur contents; with a charge of 200 per cent. lime, a metal of 0.02 per cent. sulphur contents.

These interesting data being established, it was decided to continue the electric smelting experiments on a larger scale. A stationary, rectangular furnace was therefore built of fire brick, having two carbon electrodes 4 inches square by 18 inches long suspended in the middle of the furnace, about 8 inches apart, and a current of 50 amp. and 175 volts used. The result of the first heat gave, from a charge of 32 pounds of roasted ore, 29 pounds of lime and 8 pounds coke, 9.5 pounds of metal, nicely collected in the bottom of the furnace, and showing every evidence of having been perfectly liquid before cooling, the impressions on the joints between the bricks being sharp and distinct. This furnace was followed by a larger one, with 5 inches x 17 inches crucible and a 10-inch. x 22-inch. body, provided with a tapping hole, for drawing off the slag, opposite each carbon and about 2.5 inches above the bottom. The stock was a mixture of 100 parts of ore, 150 parts of lime and 25 parts of coke, and the character of the metal obtained from these charges (*b*), as well as from the above-mentioned mixture (*a*), will be seen from the following table:

	(*a*) Per cent.	(*b*) Per cent.
Chem. composition:		
Silicon	1.07	0.23
Sulphur	0.76	0.07
Copper	0.05	0.06
Nickel	5.72	5.67
Transverse strength:		
Breaking load, pounds per square inch	813	1,642
Deflection, inches	7/64	7/32

In subsequent experiments ore screenings from partly-roasted pyrrhotite of the following composition were used:

	Per cent.
Metallic iron (mostly as sesquioxide)	50.90
Sulphur, 8.68 per cent. in (*c*), re-roasted (*d*)	5.81
Insolubles	13.96
Nickel	3.47
Copper	0.07
Phosphorus	0.003

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and the results from a couple of experimental heats (*c*), with 150 per cent. lime and 28 per cent. coke, and (*d*), with 200 per cent. lime and 25 per cent. coke, were analyzed and found to have the following composition:

	(*c*) Per cent.	(*d*) Per cent	(*e*) Per cent.
Combined carbon	....	0.05	0.81
Graphitic carbon	....	3.25	1.28
Silicon	1.79	3.97	1.35
Manganese	....	0.18	0.27
Sulphur	0.28	0.063	0.27
Phosphorus	0.037	0.039	0.008
Copper	0.045	0.075	0.02
Nickel	5.55	6.22	5.77
Cobalt	0.20	0.20	0.24
Arsenic	Trace	Trace	....

Noticing all along that the metal did not contain the expected full percentage of Ni, Co and Cu, and looking for an explanation of the same, we observed, in tearing up the bottom of the furnace, under the ferro-nickel slab and directly below the carbons, a peculiar-looking, yellow mass of a hard and brittle metallic nature, which, upon examination, was found to have the following composition:

	Per cent.		Per cent.	
Fe	28.5	Si	17.0	(Carborundum?)
Ni	40.0	C	7.3	
Co	3.5	S	0.2	
Cu	3.5	P	0.04	

The next step in the series of experiments undertaken was the construction of a *continuous* furnace, in which the metal could be produced without interruption, and from which the slag and the iron could be drawn as desired, or would flow uninterruptedly. A furnace of the type suggested and described by de Laval was at first tried, two carbons 24 inches by 4 inches by 4 inches being placed horizontally in the bottom of the furnace, the hearth provided with tapping holes for the slag below the bosh line, and with iron notches at bottom for emptying the furnace at end of "the blast," and between them the rising channel intended for the continuous flow of the metal, without being mixed with the slag.

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However, soon after starting up, the bridge between the two chambers was cut away, in spite of the water jacket, and after repeated trials and sundry changes this type had to be abandoned. The furnace mixture used in these attempts was 100 parts of ore, 120 parts of lime, and 15 parts of coke, yielding a metal of the composition as shown in preceding table marked (*e*). Remelted in a crucible and cast into test bars of 1 square inch cross section, these bars showed a transverse test of 1,941 pounds to the square inch, and a deflection of 5/32 inch.

Another type of furnace was now tried, the same having two cast-iron electrodes, 36 inches long by 4 inches x 4 inches cross section, and two coke pencils of the same size, placed horizontally and opposite one another, about 12 inches from the bottom of the furnace, and made adjustable. The cast-iron electrodes, however, did not prove suitable, melting away too rapidly, and, consequently, they were replaced by carbon pencils. In a successful run of a couple of hours, some 98 pounds of metal were made, but owing to the arc's working downward, melting away the brickwork on the side of the furnace, the operation was discontinued.

From the experience gained up to this time, we concluded that a modification of the type of furnace at first tried might prove satisfactory, and we therefore went back to it. A series of new furnaces were then constructed, which, after a run of eight to twelve hours each, were torn down and reconstructed with such improvements as were indicated by the results of the successive experiments, which culminated in the electric furnace here described:

Fig. 1, showing top view; Fig. 2, a vertical longitudinal section on line 2-2, figs. 1 and 3; Fig. 3, a vertical transverse section on line 3-3, figs. 1 and 2, and, Fig. 4, showing a horizontal section of the same on broken line 4-4, fig. 2.

The furnace body is of rectangular shape, and constructed of cast iron sides and ends, A and B, and a bottom frame, C, with an interior lining A°, B°, C°, of refractory material, the bottom lining C° being retained by a steel plate C′, secured to the frame C. The lower parts of the sides and ends and the bottom frame are water-jacketed, as shown at *a*, *b* and *c*. The end plates are provided with projecting lugs *b′*, *b″*, through which the ends of

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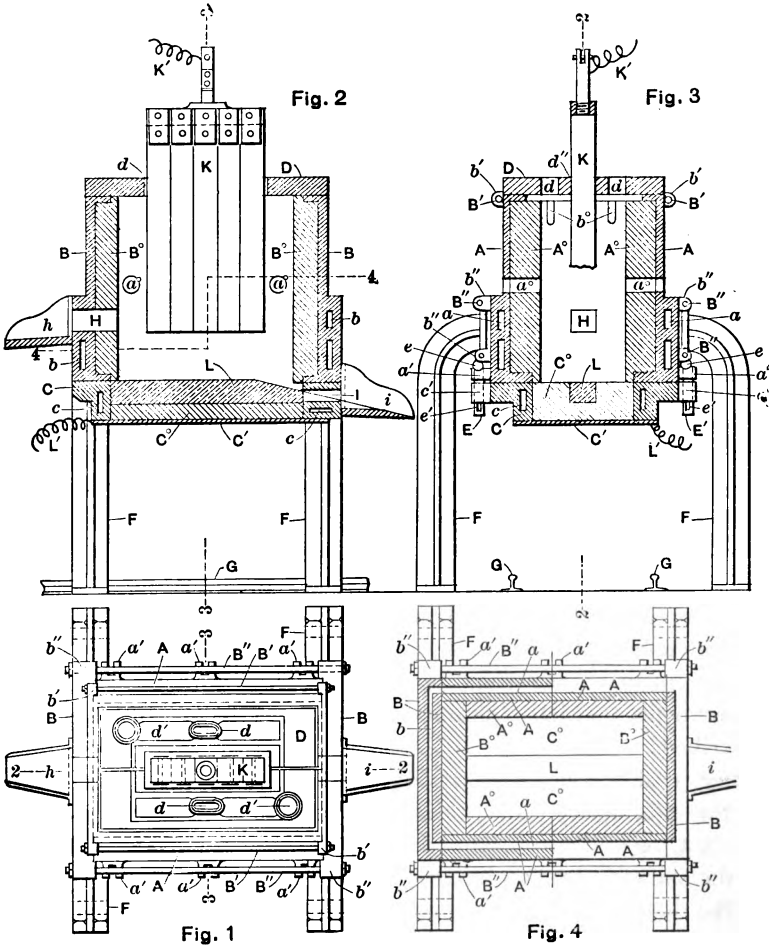
stay-bolts B′, B″ are passed, and by means of which the frame plates are bolted securely together. Another feature of importance is the exchangeable bottom. Registering slotted lugs *a′*, *c′*,



are provided on the lower parts of the sides A and the bottom frame C, respectively, and these receive cross-headed bolts E, resting with the heads *e* on the upper lugs, and being provided at the lower ends with mortices *e′* to receive wedges, driven in below

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the lower lugs, as shown in Fig. 3. One of the ends is provided with an opening H, for drawing off the slag, the same being some distance from the bottom, and provided with a spout *h*. The iron notch H, for drawing off the metal, is formed within the bottom frame C, at the end opposite to that of the slag notch and below the upper surface of the bottom lining. In the sides A A°, and above the level of the slag notch are vent holes *a*°, and in the ends stoke holes *b*°, the former enabling the escape of the gases of combustion and reduction, and the latter the breaking up of the slag crusts that may form, and for facilitating the even settling of the stock. The cover D is provided with feed and vent holes (*d* and *d'*, respectively), and besides an opening *d''* for the electrode. K and L are the upper and lower electrodes, with connecting wires K' and L', the former consisting of a battery of square carbons, suitably connected at the top and held adjustably suspended, and the latter of a carbon bar, embedded within the bottom lining and extending longitudinally from the metal notch to the end of the bottom frame, with which it is in contact. The furnace is supported by legs F, at an elevation above the floor, to make room for the ladle cars running on rails G, as well as for the convenience of readily exchanging a burnt-out bottom for a newlined one. The furnace lining is made of magnesia brick, the only material that we have found to withstand the heat and the chemical action between the charge and the lining. These bricks have the following composition:

	Per cent.		Per cent.
SiO_2	4.41	CaO	9.40
Al_2O_3	23.07	MgO	63.12

In this furnace ferro-nickel was made for several days from poorly-roasted ore (with about 3 per cent. sulphur and 53 per cent. iron) at the rate of 60 pounds per hour (equivalent to 225 gross tons per annum), with an electric energy of 108 K. W. (1,350 amp. at 80 volts) = 144 horse-power, or at the rate of 0.64 horse-power per gross ton year, or 230 horse-power per gross ton day, or about 5,500 horse-power per gross ton hour.

With a furnace of 300 to 500 horse-power, which would be more economical, 200 horse-power would probably suffice for obtaining a gross ton of ferro-nickel per twenty-four hours. At a rate of

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$10 per horse-power per annum for the power, $5 per ton for the ore, $5.50 per ton for coke, and $2.50 per ton for lime stone, the cost items for the manufacture of 1 ton of ferro-nickel pig in the electric furnace at this place would probably have been as follows:

2 tons partly-roasted pyrrhotite, @ $5	$10.00
500 pounds coke, @ $5.50	1.37
1.5 ton lime stone fines, @ $3	4.50
Labor and salaries	2.50
Electrodes and repairs	2.50
Power, 200 horse-power, @ $10	5.50
Total cost per ton metal	$26.37

The value of this product—a ferro-nickel pig with 3 per cent. nickel contents—should be that of the nickel contained in the metal, plus that of the pig iron; so that, if we assume the value of nickel at 30 cents per pound, and pig iron at $14 per ton, the product would be worth (60 x 0.30 = $18 + $13.57 =) $31.57—showing a profit of over $5 per ton metal produced.

Simultaneously with the above work, experiments in dead roasting the pyrrhotite were also carried out, and these being sufficiently encouraging to warrant the belief that this could be done at small cost, while at the same time the resulting SO_2 gas would be profitably utilized in the sulphite pulp industry, and as the electric smelting plant on the large scale intended would necessitate the completion of a large power plant, it was decided to carry out the original intention of roasting the ore, briquetting the roasted fines, converting the briquettes, and finally converting this pig metal by means of the open hearth or Bessemer process, into a ferro-nickel steel.

Although our electric smelting experiments were not carried to a final issue and did not result in establishing an electric smelting plant, they nevertheless prove the possibility, and, under certain conditions, the practicability and economy of converting ores into metal by means of the electric furnace—and so classing us among those electro-metallurgists whom a recent writer on the subject of electric smelting has designated as the "more reserved opportunists."

Sault Ste. Marie, Ont., February 10, 1904.

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A paper read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 9, 1904, President Richards in the Chair.

DISSOCIATION BY MEANS OF THE ALTERNATING ELECTRIC CURRENT.

By William H. Davis.

In presenting this paper to this Society I shall make no effort to discuss the subject-matter from a theoretical point of view; this will be left to those who are better fitted for the work.

It would be a matter of pleasure and satisfaction to me if the results were confirmed by others, and I shall therefore endeavor to present the history of the experiment in such a manner that any one who wishes may repeat it, and, I trust, prove that work may be done upon a solution by an electric current, although this is opposed to the theory of Arrhenius, as held by some workers at the present time.

In the early spring of 1902 I began a series of experiments in the cyanide plant of the Smuggler-Union Mining Co. at Telluride, Colorado, in hope of perfecting a method of recovery of cyanogen from the double salts of a cyanide solution. A chemical process seemed out of the field of profit owing to the solubility of the simple cyanides in excess of potassium-cyanide. The solution had either to be rendered acid or an excess of the precipitant added, and there being no cheap precipitant of the cyanogen, it was decided to turn to electrochemical investigation.

A direct current was first employed and it was soon found that a division of the compound sought (KCN) was the result, and that correction could not be made by placing the anode in a porous cup, for the alkali and acid radicals were constantly being separated by the current effect: therefore, if a solution of alkali, say caustic soda, was contained in the porous cup the sodium radical would pass out proportional to the entering cyanogen, and if an excess of caustic soda was maintained, even by washing the anode, a polymerization of the cyanogen would occur in sufficient amount to make the process valueless for the work at hand.

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The direct current having been found ineffectual, attention was turned to the alternating current. It was at once noticed that the desired results were obtained together with precipitation of the basic metals when an excess of free alkali was present. The determinations were made by the usual Liebig method ($AgNO_3$) and it was found that by no other known method could the cyanide content be raised higher. In the case of foul solutions the cyanide was in many cases raised 0.5 of one per cent. For final results I will refer those interested to the report of the Director of the Mint, upon the production of the precious metals in the United States during the calendar year 1902, pages 99 to 101, to be had from the Director of the Mint at Washington.

These results lead up to the consideration of the theoretical side, and in the study it was found that an alternating current would raise the osmotic pressure of a solution concentrated so that complete dissociation was not present.

The experiment was conducted in the following manner: A porous cup holding about 200 c. c. was rendered semi-permeable with copper-ferrocyanide and the walls so adjusted that the cup would maintain a hydrostatic pressure of one cm. above the water level outside the cup (several trials were made before this adjustment was reached). A rubber stopper with two holes was then placed securely in the cup, through one of which holes a glass tube was inserted, one square mm. in cross-section, reaching within 1 m m. of the bottom of the cup, and through the other hole another tube was inserted reaching only to the bottom of the stopper; the whole was then sealed with sealing wax and placed in a beaker of distilled water, wires of platinum were placed in the tubes, which served as electrodes, either of these wires reaching to the bottom of its respective tubes, and these were connected to a switchboard. Through the tube reaching to the bottom of the cup a 10 per cent. solution of sodium acetate was led into the cup until the height in the tubes indicated 10 cm. above the water level outside the cup, and then the apparatus was allowed to stand for twenty-four hours. At the end of this time the solution stood 1 cm. above the water level, and then 2 ampères of alternating current were sent through the solution. No changes were made excepting to close the switch. In five seconds the solution rose to 5 cm. and would not go higher

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during the next thirty seconds. The current was then turned off and the solution fell to the initial height in about twenty minutes. The current was again turned on and the same results followed, and this was gone through with perhaps 20 times during the week or ten days following.

The current was from a three-phase generator of the usual type, working at 60 cycles per second; one leg of the circuit was used and the current was controlled by a bank of incandescent lamps connected in multiple.

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NOTES ON THE INDUSTRIAL ELECTROLYSIS OF WATER.

BY W. S. LANDIS.

In view of the existing work already published on the subject and the remarkable development of electrochemistry along industrial lines in this country, there may seem to be little call for a paper such as this. Still there are a few scattered references and comparisons which may interest some of our members.

Besides a number of articles which have appeared in various foreign and domestic periodicals, we have at least two works devoted to this subject. The first, "Die industrielle Elektrolyse des Wassers," by M. U. Schoop, not translated. This small pamphlet describes only systems which have demonstrated their commercial practicability by actual installations, and also deals with compression, storage and use of the gases. The second, "Elektrolyse des Wassers," by V. Englehart, and translated into English by Dr. J. W. Richards, is a very complete and valuable addition to our knowledge of the subject.

Electrochemically, the apparatus for the production of hydrogen and oxygen from water may be divided into two classes, viz.: those using acid electrolytes and those using alkaline electrolytes. In the former case the electrodes are universally of lead, although platinum has been proposed. It is self-evident that the cost of platinum, even if used only as a thin plating, is such as to prohibit its use on a commercial scale. Iron is the material generally used with the alkaline electrolytes. As to the relative advantages of these two materials, there seems to be a great difference of opinion. To enumerate all the arguments for and against either would be beyond the scope of this paper. A few of the requirements which the material must fulfill are:

1. It must be unattacked by the electrolyte or the products of decomposition.

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2. It must be rigid, so as not to be easily deformed and so cause annoying short circuits.

3. It must be commercially available for large installations without necessitating exhorbitant interest charges.

As to the form of apparatus, I will refer to the two books already mentioned. The apparatus must be designed so that there is no possibility of the mixing of the two gases. This is accomplished either by keeping the two electrodes separate in separate vessels or by the use of a porous or solid diaphragm. An interesting case of the use of metal as a diaphragm is found in the apparatus of Garuti. He uses a partial metallic diaphragm and by keeping the electromotive force between the electrodes less than

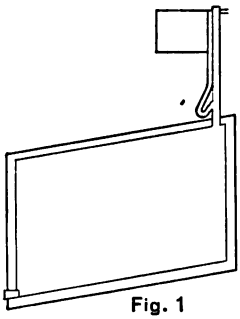

Fig. 1

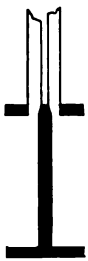

Fig. 2

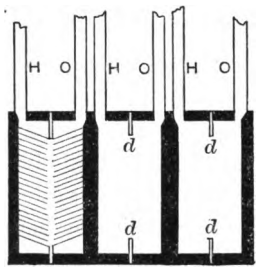

Fig. 3

twice that required for decomposition prevents it from acting as an electrode. The other diaphragm materials are asbestos and clay.

A form of apparatus not described in either of the two references cited is that designed by Prof. W. S. Franklin, Lehigh University. So far as I have been able to ascertain, this is the only apparatus designed in this country which has been used on a commercial scale. It was never patented, and at the present time is used by the Nernst Lamp Co., Pittsburg, Pa. The apparatus consists of a number of massive frames of cast iron of which Fig. 1 is a side view, Fig. 2 is a section and Fig. 3 an assembly. The frames are bolted together and separated from each other by partial diaphragms of sheet rubber, such as is used for steam packing. The gases are prevented from mixing by breaking up the compartments with a large number of thin iron strips, as shown in the figure. Each compartment is supplied with a reser-

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voir for the electrolyte and the gases are led off through the tubes marked H and O. The two end castings are connected to the source of the current.

The current used in the apparatus varies with the size of the opening in the rubber diaphragm. With this opening, 13 x 19 centimeters, a current of about 25 ampères is employed. A higher current than this causes a mixing of the gases. The voltage absorbed per compartment is about 3.8, giving an efficiency of about 38 per cent.

A more complete description of the cell and its working may be found in *Physical Review,* Vol. IV, No. 19.

A comparison of the cost of producing oxygen and hydrogen by other methods with the electrochemical is hardly to be attempted, because of the many different conditions surrounding the two cases. In the first place it is impossible to obtain the gases on a commercial scale, either by physical or chemical methods, in such purity as furnished by the electrochemical processes. On this account a comparison is useless save as a mere approximation. Taking as a basis for the electrochemical processes, power costing $50 per kilowatt-year, the cost of producing a cubic meter of mixed gas, that is ⅔ hydrogen and ⅓ oxygen, is about 4 to 6 cents. This includes interest and sinking fund on the cost of plant. To produce the same amount of gas from zinc and sulphuric acid and barium peroxide will cost about 40 cents; all the chemicals being based on market prices about March 15, this year. In this comparison the qualities of the gases are not taken into account, a still further advantage on the side of the electrolytic production. The figures for the production of electrolytic gas are taken from the report of the plant of the Italian Government used for supplying hydrogen for ballooning to the Italian army.

About the only serious competitor in the field of oxygen production is the Linde method of preparing oxygen from liquid air by evaporating off the nitrogen. The product obtained by this method contains only about 50 per cent. oxygen. As this material can be produced for from 1 to 2 cents per cubic meter, it can be seen that it is quite a serious competitor. Of course, where there is a demand for both hydrogen and oxygen the electrolytic process has the advantage.

So far as I have been able to ascertain there are in this country

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but two installations for the commercial production of oxygen and hydrogen electrolytically. The one is at the Chloride Accumulator Co's Works, at Philadelphia, and the other at the works of the Nernst Lamp Co., Pittsburg. Several laboratories of technical schools are supplied with small plants, in general designed by a person connected with the institution, but in most cases their cost and low efficiency would prohibit their use commercially.

With the great advantages of the electrolytic apparatus and its products, it seems very strange that a more general introduction has not taken place in this country, the home of applied electrochemistry.

Metallurgical Laboratory,
Lehigh University.

DISCUSSION OF A PAPER ON THE ABOVE SUBJECT AND COVERING THE SAME GROUND, READ BY DR. J. W. RICHARDS BEFORE THE NEW YORK SECTION OF THE SOCIETY, JANUARY 26, 1904.

MR. CARL HERING: I should like to ask Professor Richards whether in his researches on this subject, he has found any data showing whether water is electrolyzed at a lower voltage when near the boiling point; that is, whether heating the water will lessen the amount of voltage required to decompose it. It would seem as though water ought to be more easily decomposed the higher the temperature. If that is the case, it might be even more economical to keep the liquid near the boiling point.

I should also like to ask whether he has found anywhere an answer to the question where the energy comes from that is represented by the expansion of the gas from the volume it had in the water, to the volume it has as gas. The increase, I believe, is about 1,600; that is, one cc. of water will make about 1,600 cc. of gas. The question is, does the energy represented by this expansion come from the electric energy, or, as some think, is it abstracted in the form of heat from the water and from the surrounding gases.

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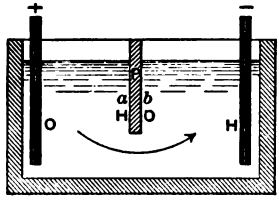
MR. T. WOLCOTT: I should like to ask as regards the metallic partition. If I understand the description of the metallic partition it is like this (sketching on blackboard): The partition P, does not reach to the bottom. The bulk of the current would pass below the partition, as indicated by the arrow. This current, of



course, produces oxygen at the anode and hydrogen at the cathode, but no gases at the partition. A current going through the partition from *a* to *b*, would ordinarily produce hydrogen at *a* and oxygen at *b*, but in this case no gases are produced on the partition. Is that correct?

DR. J. W. RICHARDS: Yes.

MR. WOLCOTT: Now I can understand how the current can go below the partition without producing oxygen on the *b* side of the partition or elsewhere in the cathode compartment, or hydrogen on the *a* side of the partition or elsewhere in the anode compartment, but it is not clear to me how the current can pass through the partition without producing gases at *a* and *b*.

DR. RICHARDS: It does not go through. As a matter of fact an insulating partition would be just as good as the metallic, but at the voltage of the cell the metallic partition is not a conductor.

DR. E. F. ROEBER: There is absolutely nothing new in it. He speaks always of a conducting partition; it is not conducting, it is exactly as if it were glass.

MR. G. W. FLETCHER: I should like to ask why the metallic partition should not extend to the bottom? Suppose that were a block of metal, your resistance between electrodes would be much less, and I do not see why it is not a conductor.

MR. REED: If there is no way for the current to get around the plates, it will go through, but the resistance would be much less through the solution, although that is a metallic partition and has a greater electric conductivity than the solution has. It is

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not the electric conductivity altogether that determines the passage of the current. The current could not pass through an inert metallic diaphragm without overcoming a counter electromotive force at the surface of the diaphragm. In this case it would take about 2½ volts to force the current through, the diaphragm being of metallic lead at the beginning, but being soon converted into lead peroxide on the surface acting as anode.

MR. HERING: The subject of making that diaphragm very thick, was discussed in this very hall last April in a paper by Professor Bancroft, published in our Transactions. He made the diaphragm excessively thick and brought it close to the two electrodes.

VICE-PRESIDENT DOREMUS: Professor Richards referred to the experiments of Troostwyk. Those experiments were repeated by Pearson, and reported in the Philosophical Transactions, Vol. XC, page 188, 1797. It is an extremely interesting paper. Thousands and thousands of electric sparks were passed through the water and the constitution of the water determined by analysis of the gases freed. That was quite some years ahead of the invention of the voltaic cell, and before the experiments of Nicholson and Carlisle. I tried last year to get in this city the original papers of Nicholson and Carlisle on this subject, but they were not available. I feel somewhat of the opinion that perhaps they had tried the experiments before Ritter. Nicholson was an inventor and very skilled in his work; Carlisle was a surgeon—a very curious combination of two people in that early time in the work of electrolysis. I think now we can hear from Professor Richards in answer to Mr. Hering.

DR. RICHARDS: I will say that I took the statement that Ritter had seen the decomposition of water by the voltaic pile before Nicholson and Carlisle, from *Ostwald's Elektrochemie.* Perhaps Ostwald was wrong, but he is convinced that Ritter was the first to publish the experiment. It was in the same year, 1800. In reply to Mr. Hering's remarks about the high temperature, he gives practically the view of Siemens and Halske, who state that less voltage is required to run the apparatus if it is run at 70° C., than if at lower temperature, and they recommend that the apparatus be heated to 70 degrees before the current is put in, in order to save the loss of current which would be used in heating it up to that temperature.

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MR. HERING: Why not heat it still higher?

DR. RICHARDS: 70° C. is fairly towards the boiling point, and I think the vaporization of the solution where it was not completely covered might cause trouble. With the apparatus packed in sand, it keeps itself at that temperature and works at lower voltage. As to whether the energy of the expansion of the gases comes from the electric current, or where it comes from, that is a theoretical question which it would take a long time to discuss. I think probably the electric current has in the end to furnish the energy, though not directly.

Now with regard to this partition which has been spoken of. This is the apparatus of Garuti, who first made application of the fact that a metallic partial partition could be used in place of the non-conducting partition, and the advantage of using a metallic partition is, of course, its strength and its not being so easily broken. So that if the partition were complete it would take a voltage of at least three volts from pole to pole to start the current passing through the two salts which you have, but if the partition is incomplete, then at a voltage of less than three the current can pass from anode to cathode, and the current necessarily passes under the partition and none of it goes through. Under these circumstances the metallic partition is just as good as a non-conducting partition of earthenware or glass. I understand that Garuti and del Proposto were the first ones to make application of the fact, and to use a metallic partition where others had not thought of using it, and using it in the sense of a non-conducting partition.

MR. REED: It seems to me the question of the origin of the energy involved in the expansion of the gases is one that ought not to be so difficult to determine, when we consider the energy of the reaction. In the first place a gas cannot be evolved in the gaseous state by electrochemical action (because it is not a conductor, and an ion must act as a conductor), as it must transmit the current. Consequently these gases, when they are evolved, must be deposited in a liquid state. They must, in other words, be deposited as oxygen and hydrogen in solution. We know that they are soluble and we know that the solution contains them dissolved, and that is the only way they can act as conductors. In other words, it is only in solution that gases can transmit the

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current electrolytically. We know, at least, that the gases deposited at the beginning of the passage of current will be dissolved until the liquid is saturated with the gases, and I see no reason for believing the action to be different after saturation. What occurs after saturation is simply the evolution of gas by a supersaturated solution in a manner identical with that of the evolution of carbon dioxide from a saturated solution. The supersaturation of a liquid by gases in electrolysis extends necessarily only to a thin layer of solution in immediate contact with the electrodes. For this reason the gas evolved from the supersaturated solution around the electrode appears as bubbles in contact with the electrode and becomes attached to it, exactly as bubbles of CO_2, evolved in a glass of "soda water" against the sides of the glass, become attached to the glass and appear to be evolved from it.

To me there appears to be no more reason for supposing that gases are evolved electrolytically in bubbles, that is, in the gaseous state, than for supposing that the bubbles of CO_2 on the surface of a tumbler, containing a saturated solution, come out of the glass instead of the solution. The evolution of the gas from solution is a purely physical action and has nothing to do with the electrochemical action, which precedes it. There is a continual evolution of gas from the supersaturated solution, and, consequently the energy required to produce that gas must be absorbed from the heat of the surrounding liquid.

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TRANSACTIONS

OF THE

NEW YORK SECTION

PAPERS READ AT THE MEETING OF JANUARY 26, 1904, AND THE DISCUSSIONS THEREON.

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A paper read before the New York Section of the American Electrochemical Society, New York, January 26, 1904, Vice-President Doremus in the Chair.

THE THERMO-CHEMISTRY OF ELECTROLYTIC DISSOCIATION.

By C. J. Reed.

In a paper read at the last general meeting of this Society, and published in Vol. IV of Transactions, Dr. Joseph W. Richards has endeavored to show that neutralization heat is merely heat of condensation of vapor of water from the gaseous to the liquid state. From the circumstance that there is no quantitative relation between the formation heats and the solution and dilution heats of compounds he concludes that ionization cannot be a destruction or dissociation of the compound. Throughout his paper he emphasizes the assumption that ions in solution are in the combined instead of the dissociated state.

Immediately following this assumption he assumes that in the dilute solution of $2NaOH.400\ H_2O$, the NaOH exerts an osmotic pressure of 12.34 atmospheres, which is about twice the osmotic pressure that would be exerted if the Na and the OH were combined, and is equal to the osmotic pressure that would be exerted if the NaOH were completely dissociated. His conclusions all depend upon this assumption, that the osmotic pressure is that which would be produced by complete dissociation.

Being unable to understand these statements, I wrote to Dr. Richards for an explanation. In reply he wrote as follows:

"The osmotic pressures are calculated on the assumption that the solutions are sufficiently dilute for what is called 'complete ionization' to have taken place, that is, for the osmotic pressure to have reached a value twice as great as would be calculated for the normal gaseous pressure of the salt occupying the given volume." Continuing he says, "If I had the real measured values of the osmotic pressure of NaOH, I would have used them, but these being lacking, they can be calculated on the assumption that in such a good electrolyte it would be two times the theoretical pressure of gaseous NaOH at that temperature and value."

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In assuming that the osmotic pressure is doubled by diluting to complete ionization, he has assumed that there is complete dissociation or separation of the ions, as it is only on this supposition that the osmotic pressure could be doubled. Therefore, Dr. Richards' proof that there is no dissociation in dilute solutions, rests upon the fundamental assumption that there is complete dissociation in such solutions.

It appears also from his letter that this value of 12.34 atmospheres is not based on anything more than a mere supposition that his fundamental supposition is erroneous.

Two pages of thermochemical constants are given which are based on an arbitrary assumption that a mercuric sulphate electrode has an electromotive force —0.89 volt, and that Hg has a thermochemical constant—20,500 calories, two values which, according to his own rule, are not consistent with each other. According to the method given by him of finding formation heats, that of $HgSO_4$ would be 107,900 — 20,500 = 87,400 calories, equivalent to an electromotive force of 3.76 volts.

Why his table of thermochemical constants is based upon this assumption is not apparent. An inspection of his tables shows that the formation heats derived, according to the method described, do not in general agree with those actually observed. It is true there is an agreement among a considerable number, particularly the chlorides of the alkali metals. As we get further away from the alkalies and further away from the chlorides in the list, we find the disagreement more marked. I have not made a comparison of all the different compounds whose formation heats have been determined, but have picked out at random a sufficiently large number, in which the disagreement is great, to show that the law does not hold. Many compounds whose formation heat is positive and large, are, according to Dr. Richards' rule, negative. The following list shows in parallel columns some of these formation heats:

	BERTHELOT.	RICHARDS.	DIFFERENCE.
$CuCl$	35,400	22,700	— 12,700
$CuCl_2$	62,500	68,800	+ 6,300
$PbCl_2$	77,900	85,400	+ 7,500
$TlCl$	38,400	42,300	+ 3,900

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	BERTHELOT.	RICHARDS.	DIFFERENCE.
$HgCl_2$	50,300	39,600	— 10,700
HgCl	31,320	— 0,700	— 32,020
AgCl	29,000	13,900	— 15,100
Ag_2Cl	29,500	— 12,100	— 41,600
$SnCl_4$	158,300	163,200	+ 4,900
KBr	90,400	94,200	+ 3.800
$MgBr_2$	172,000	173,200	+ 1,200
$PbBr_2$	63,700	65,400	+ 1,700
TlBr	45,100	35,200	— 9,900
$HgBr_2$	44,600	25,400	— 19,200
HgBr	28,200	— 7,800	— 36,000
AgBr	27,100	7,000	— 20,100
$AuBr_3$	16,700	6,000	— 10,700
$PtBr_4$	67,100	51,400	— 15,700
$SnBr_4$	129,400	134,800	+ 5,400
KI	81,800	75,100	— 6,700
LiI	82,800	76,100	— 6,700
NaI	77,400	70,400	— 7,000
SrI_2	157,000	143,800	— 13,200
CaI_2	148,600	173,400	+ 24,800
CdI_2	61,500	44,400	— 17,100
CuI	23,700	— 3,500	— 27,200
PbI_2	53,400	27,000	— 26,400
MgO	143,400	150,100	+ 6,700
FeO	68,900	63,300	— 5,600
FeS	24,000	15,800	— 8,200
CoO	64,100	57,900	— 6,200
NiO	61,500	56,900	— 4,600
ZnO	84,800	75,900	— 8,900
ZnS	43,000	24,200	— 18,800
ZnSe	30,300	— 14,000	— 44,300
NiS	19,500	5,200	— 14,300
CoS	21,900	10,400	— 11,500
CoSe	9,900	— 2,400	— 12,300
NiSe	9,900	— 20,400	— 30,300
CaSe	58,000	73,000	+ 15,000
SrSe	67,600	81,600	+ 14,000
MgS	79,400	98,400	+ 19,000

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	BERTHELOT.	RICHARDS.	DIFFERENCE.
MnS	45,600	39,600	— 6,000
MnSe	22,400	14,000	— 8,400
FeS	24,000	11,600	— 12,400
FeSe	16,000	— 14,000	— 30,000
CdO	66,300	59,400	— 6,900
CdS	34,400	7,800	— 26,600
CdSe	23,700	—117,800	—141,500
Cu_2O	43,800	8,000	— 35,800
CuO	37,700	25,600	— 12,100
CuCl	35,400	22,700	— 12,700
$CuCl_2$	62,500	68,800	+ 6,300
Cu_2S	20,300	— 43,600	— 63,900
CuS	10,000	— 26,000	— 36,000
Cu_2Se	8,000	— 69,200	— 77,200
CuSe	17,300	— 51,600	— 68,900
PbO	50,800	42,800	— 8,600
$PbCl_2$	77,900	85,400	+ 7,500
PbS	20,300	— 9,400	— 29,700
PbSe	17,000	— 35,000	— 52,000
$PbSo_4$	215,700	214,800	— 900
H_2S	9,500	— 12,000	— 21,500
H_2Se	— 15,800	— 37,600	— 21,800
TlOH	39,600	58,100	+ 18,500
Tl_2O_3	87,600	131,600	+ 44,000
TlCl	38,400	42,300	+ 3,900
TlBr	45,100	35,200	— 9,900
TlI	37,000	15,100	— 22,000
TlF	52,000	54,800	+ 2,800
Tl_2S	21,700	— 6,400	— 28,100
Tl_2Se	13,400	— 32,000	— 45,400
HgO	21,500	2,200	— 19,300
$HgCl_2$	50,300	39,600	— 10,700
HgCl	31,320	— 700	— 32,020
$HgBr_2$	44,600	25,400	— 19,200
HgBr	28,200	— 7,800	— 35,000
HgI_2 yellow	35,800	— 12,800	— 51,600
HgI_2 red	38,800		
HgI	21,250	— 26,900	— 48,100

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	BERTHELOT.	RICHARDS.	DIFFERENCE.
HgS black	10,600	— 49,400	— 60,000
HgS red	10,900		
HgSe	6,300	— 75,000	— 81,300
HgSO	165,100	174,800	+ 9,700
Hg_2SO_4	175,000	133,800	— 41,200
Ag_2O	7,000	— 9,200	— 16,200
Ag_4O_3	21,000	24,800	+ 3,800
AgCl	29,000	13,900	— 15,100
Ag_2Cl	29,500	— 12,100	— 41,600
AgBr	27,100	7,000	— 20,100
AgI	15,600	— 12,100	— 27,700
Ag_2F	23,900	— 1,400	— 25,300
Ag_2S	3,000	— 60,800	— 63,800
Ag_2Se	2,000	— 86,400	— 88,400
Ag_2SO_4	162,600	163,400	+ 800
Au_2O_3	— 11,500	— 57,600	+ 45,100
$AuBr_3$	16,700	6,000	— 10,700
PtO	17,900	— 38,200	— 56,100
$PtBr_4$	67,100	51,400	— 15,700
PtI_4	43,600	— 25,000	— 68,600
$SnCl_4$	158,300	163,200	+ 4,900
$SnBr_4$	129,400	134,800	+ 5,400
K_2CO_3	285,300	288,700	+ 3,400
Li_2Se	93,700	90,000	— 3,700
$ZnCO_3$	194,200	199,300	+ 5,100

I would call attention to the element thallium, which in his table of thermochemical constants is marked as a dyad. I have been unable to find any compound in which it exists as a dyad.

That there is some additive relation existing between the chlorides of many metals and the corresponding iodides and bromides is a fact which has been known for a long time, and which was mentioned by me in a paper read December 20, 1900, before the Franklin Institute. What this relation is does not, however, appear to have been determined.

If we were to accept Dr. Richards' conclusions, it would be merely a matter of arithmetic to determine the formation heats of all compounds after having determined the formation heat of a single compound of every element.

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Starting with his assumption, that the thermochemical constant of mercury in mercuric salts is —20,500, the formation heat of mercuric chloride gives us by subtraction the thermochemical constant of chlorine for all compounds. From this and the formation heat of potassium chloride we could obtain the thermochemical constant of potassium for all compounds, and so on. Unfortunately this simple method breaks down very soon, as is amply shown in the above list of formation heats.

Dr. Richards will probably reply by saying that many of the substances mentioned in this list are insoluble, and that his law applies only to salts in solution. It is admitted that a number of these salts are comparatively insoluble in water. In those cases it is only necessary to take into account the latent heat of fusion, which in all cases will be found to be very small. We must not suppose, however, that because a salt requires a large quantity of water to dissolve it, even a much greater quantity than the 400 molecules, that it is, therefore, to be excepted from any law relating to its formation heat. Dr. Richards might, for instance, consider lead chloride an insoluble salt simply because it requires 200 times its weight of cold water, or 30 times its weight of hot water to dissolve it. This sparing solubility, however, does not affect the formation heat of the substance in solution. Such an argument is seen not to hold on examining the tables. Lead sulphate, for example, is one of the most highly insoluble salts, and yet it is one of those in which Dr. Richards' method agrees most closely with experiment, differing by only about ½ per cent. Silver sulphate is another comparatively insoluble salt which agrees within about ½ per cent. It cannot be claimed that an undue proportion of the exceptions are insoluble.

DISCUSSION.

Dr. J. W. Richards: I must say I do not like to pose altogether as the champion of the rule which Mr. Reed ascribes to me, and which Tomassi claimed as his discovery some twelve years ago, and which Hess, one of the founders of thermochemistry, formu-

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lated, as to the law of the equilibrium of salts, so I disclaim being the inventor or discoverer of this rule. The rule is one which has been debated and talked about a great deal in thermochemistry. The principle is, that in dilute solutions the heat of formation appears to be an additive quantity, or to depend only upon the base and the acid which are present, both contributing their quota to the heat of formation of the compound, so that when you mix two different salts there is practically very little heat evolved, and you have the principle of thermoneutrality. Mr. Reed has not made the comparisons in the sense in which they are always understood to be made, that is, of dilute solutions. He has picked out the insoluble salts which do not go into solution, and takes their heats of formation in the solid state and applies the law which is supposed only to apply to dilute solutions. I had an anticipation that Mr. Reed might be bringing forward some such heats of formation, so I brought along some figures, too. My tables do not give all that Mr. Reed quoted, but I find 27,000, for instance, given for silver bromide in a solid state, not in state of solution, because it is insoluble. So I think that most of the inconsistencies and large differences which Mr. Reed has found come from the taking of solid salts instead of salts in solution. I am cognizant of the fact that when you apply this rule to all salts that do go into solution, there are exceptions, particularly the salts of lead, and those exceptions have been ascribed to incomplete ionization of the salt in solution. Whether that is the true explanation or not I do not know. There are some cases in which the rule does not hold; in the majority of cases it does hold. It is all based on this observation, that between the heats of formation of the chlorides, for instance, of two metals, there will be the same difference as between the heats of formation of their bromides, and the same difference exists between the heats of formation of their iodides; so there is a constant difference ascribable to the bases and a constant difference ascribable to the acids, but it does not hold for insoluble salts, and there are some exceptions among the soluble salts.

Taking up the other point which Mr. Reed has brought up, he says that in my calculation of the osmotic pressure of the dissolved salt in the dilute solution I calculated on the assumption that it was completely ionized; I perhaps used that term, but not

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with the intention of saying that I believed the salt was ionized, in the ordinary sense of the term. What I meant to say was that if we assumed the salt to be ionized it would probably give twice the calculated osmotic pressure which the gasified salt should exert in the same space. There is no admission of the fundamental accuracy of the dissociation theory in making that assumption. In making experiments with dilute sodium chloride the osmotic pressure is found to be double that which undissociated sodium chloride would exert in the same space. The dissociation theory ascribes that to dilution, but without any theory at all, I would say, assuming the same thing to hold true, that the osmotic pressure of the caustic soda would be double that which is calculated. I do not see that we are admitting in that the fundamental theory. I simply make a calculation as to what the osmotic pressure would be if you applied the rule to other soluble salts, without intending to assume the fundamental theory at all.

MR. C. J. REED: I anticipated that Dr. Richards would refer to insoluble compounds, but what is an insoluble compound? One which is not dissolved in a small quantity of water? A compound is soluble if it goes into solution with hydrochloric acid. There are other solvents besides water, and a large number of these compounds are soluble even in water, in the quantity of water which should be used. Lead chloride is often spoken of as insoluble, but it is easily soluble in a sufficient quantity of water, 400 of water to 1 of lead chloride. It seems to me there is no such thing as insolubility considered in this sense. The mere fact that certain substances require a large quantity of water to dissolve them does not make any difference in their formation heats. There is a marked difference between an insoluble substance and a substance which is not dissolved in a small quantity of water. Dr. Richards assumes an osmotic pressure, which he supposes would be produced by infinite dilution, that is, by an infinite quantity of water and a finite quantity of salt. At this dilution, glass, quartz and all other compounds, so far as we know, are completely soluble in water.

The main point in the paper which Dr. Richards read, and which I understood to be new with him, was the theory that the heat of neutralization was due to the condensation of a molecule of water from the gaseous to the liquid state. I understand that

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to be Dr. Richards' theory, and I was not aware that it had been put forward before by any of these other authors he speaks of. In order to have that theory hold, it is necessary that the calculations given in Dr. Richards' paper should be based on the osmotic pressure which he has given, namely, twice the osmotic pressure which would be exerted by a molecule in a combined or undissociated state. To get the results Dr. Richards has worked out, this osmotic pressure must be doubled. Now there is no apparent excuse for doubling that osmotic pressure except the one which is given by the advocates of the theory of dissociation, viz., that there is double the number of particles produced by infinite dilution. The point I wanted to bring out is the inconsistency of the two suppositions in this theory.

DR. RICHARDS: The calculation which I made was that the heat of neutralization was equal to the condensation of the molecule of water from the gaseous to the liquid state, and since the larger part of that heat of condensation is the latent heat of evaporation, the pressure under which it is before it condenses bears only a small part in the total value of the calculation. It was not necessary to give anything but an approximate calculation, consequently I assumed double the osmotic pressure. The latent heat of vaporization at no pressure at all amounts to about 12,000, and the correction for the pressure under which the atoms were assumed to be before they condensed, amounted to, I believe, 1,500, making a total of 13,500, agreeing with the heat of neutralization. Now if, as Mr. Reed says, I had no grounds for assuming that the osmotic pressure would be double that which would be calculated —if I had assumed it, it seems it would have made a difference of only about 1,000 out of 13,500, as the larger part of the heat calculated was the latent heat of evaporation, and the question of taking the pressure into account amounts only to a correction. I hope Mr. Reed does not confound this idea of mine with the additive relation of the heats of formation. That is the law of thermoneutrality of Hess, which simply comes in in some ways to support my general position, but is not original with me.

MR. REED: In this paper Dr. Richards has shown a remarkable coincidence which I understand to be the basis of his conclusion. He works out the theoretical heat of neutralization on his theory of condensation and gets it 13,700, while the actual heat of

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observation is 13,740, which you see is very close. Now the part which he says does not count for very much, namely, that due to osmotic pressure, is 3,590. He says this is not important, and that it was only necessary to figure approximately. I thought from the calculation he had that he considered the close agreement quite important.

DR. RICHARDS: May I ask Mr. Reed whether he does not believe that the osmotic pressure of caustic soda in dilute solution would be about what I calculated?

MR. REED: I have no reason to believe it. You say it has never been determined, and you have assumed this simply because it will bring out these figures. You admit it has not been determined, and that these calculations are based on the assumption that it would bring this result.

DR. RICHARDS: I made the calculation first and formed the conclusion afterwards.

MR. H. A. JACKSON: Professor Richards' paper having been brought into the discussion, it is perhaps well to remark that in Professor Richards' calculation, showing that the heat of condensation of water under certain conditions is equal to the observed heat of neutralization of a base and an acid, and which heat therefore cannot be chemical in its nature, but a mere physical change of state, the "correction" for outer work introduced by Professor Richards is not such a small portion of the total quantity, as he has just stated, in amount so small that a slight error in its calculation would not affect the general result. But it is, in fact, 3,590 calories out of 13,700, or 26 per cent. of total. It is indeed the whole difference between the latent heat of vaporization of water and heat of neutralization, two quantities so dissimilar that I am unaware of any previous attempts to explain heat of neutralization on this physical basis. So then it would seem that the main part of Professor Richards' proof of his theory is this heat due to outer work. In calculating this in the very example given by Professor Richards I have been unable to obtain his results. The reaction cited is that of 2NaOH and 2HCl in 800 molecules of water to form 2NaCl and $2H_2O$, the heat liberated being 27,380 calories, or 13,740 for each molecule.

The osmotic pressure of the ions which disappear is, according to Professor Richards 6.19 atmospheres. Since this is 6.19 times

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normal pressure of one atmosphere, the outer work is, according to Professor Richards, 6.19 times that based on normal pressure. But the volume of our solution, 800 H_2O having a volume of 14.4 liters is much less than the normal volume of 22.4 liters on which RT = 2T calories is based. The calculation must be, therefore, not with the ratio of pressure alone to normal pressure, but with the ratio of product of pressure and volume to product of normal pressure and volume, giving

$$\frac{6.19 + 14.4}{1 + 22.4} = 2T \text{ calories} = 4 \times 2T = 8T \text{ calories.}$$

But since for any given gas the product of pressure and volume is a constant, the external work required in formation of a gas is independent of the pressure, is a constant and for 1 molecule equal to 2T calories. This calculation is merely a reversal of that used by Professor Richards to obtain the osmotic pressure in the first place. It is therefore unnecessary, and we can obtain outer work directly by inspection. The chemical equation shows we are dealing with the formation of two molecules H_2O and each molecule from the ions H and OH′, hence as each gaseous molecule requires 2T calories the work is given directly by $2 \times 2 \times 2T$ calories = 8T calories or 2,328 calories instead of the 3.090 obtained by Professor Richards. This is independent of the concentration. The 10,110 calories to which this is added is stated by him to be for 1 molecule or 18 parts H_2O. Therefore, 2,328 calories for 2 molecules gives 1,164 or 1. To which added the latent heat of 10,110 gives a total of 11,274, leaving 2,466 unaccounted for by Professor Richards' theory.

Dr. Richards: I shall go over my calculations again and see if I find your point well taken.

DISCUSSION COMMUNICATED AFTER ADJOURNMENT, BY HENRY ASKEW JACKSON.

There has been brought forward by Professor Richards, in a paper read at the last general meeting of this Society (Transactions IV, page 137), a rather new consideration of the state

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of a compound in aqueous solution which is in some particulars at variance with the at present generally accepted views based on the theory of electrolytic dissociation. Professor Richards' theory has arrested attention owing to a remarkable agreement of some numerical results as calculated by him with the observed heat of neutralization, a phenomena his theory explains on a physical rather than on a chemical basis. As the writer has been unable to come to the conclusions arrived at by Richards and is further unable to obtain the numerical confirmation of Richards' theory even in the case cited and with the data supplied by him, he feels it necessary to draw attention to the facts on which the theory is based and to these calculations in which there seems to him to be an error on the part of Richards in the application of some fundamental gas laws.

Professor Richards has developed his ideas from the standpoint of pure thermochemistry and it is necessary to see how far such data justify him in the conclusions he has reached. If we take into consideration dilute solutions, and it is to these that this discussion is confined, the most striking fact, perhaps, is the principle developed by Hess in 1840, known as the thermoneutrality of salt solutions. That is, if we mix say a dilute solution of sodium chloride with say a solution of potassium nitrate, no thermal changes are observed. No reaction as far as indicated by thermal effects takes place. Our resulting solution is identical, as far as any means at our present disposal is capable of determining, with a solution made by starting with corresponding quantities sodium *nitrate* and *potassium* chloride. The dissociation theory pictures the two salts each almost completely dissociated into its component ions, no reaction is indicated on mixing, as none occurs. In the final solution the four ions continue their separate existence as before. In other words, the heat of formation of a compound in the dissociated state from the free elements may be considered, as Ostwald has shown, to be the sum of two quantities, each depending on its respective ion and constant for that ion. It would necessarily follow that in tabulating these heats of formation of various salts certain regularities must occur, the salts of potassium will differ from the corresponding sodium salts by a constant amount, the chlorides by a constant difference from the bromides. In looking over such a table, where

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these regularities show the heat of formation so beautifully to be an additive quantity, we would naturally say that a salt in dilute solution is, certainly compared to itself in the solid form, in what we might call an ideal condition, that is, an ideal condition in so far that it obeys simple laws, and that the element in passing from the free state into this ideal condition gives up a definite amount of heat independent of the other ion with which it is combined.

It does not necessarily follow, however, that this ideal state of an element is its final state or the state of utmost combination into which it is possible for it to go. It is true that each element in passing from the free state into this condition in solution does give up this definite quantity of heat which has been called by Ostwald the heat of ionization, but that this heat is the largest amount such an element can give up, that it has then reached a state of final and complete combination is not a logical inference from these premises. So much the more, as the regularities in the heats of formation, the heats of ionization characteristic for each element are fully and better explained by the conception of dissociation in solution. They fit so well in with that theory that they not only are clearly explained by its aid, but they themselves form one, though only one, of the grounds to which it owes its support.

Richards' theory then depends on how far he is justified in rejecting the theory of dissociation on the ground that the idea of dissociation is impossible, owing to the fact that any heat of dissociation is very slight compared with the total heat of formation of compounds; and, again, how far he is justified in substituting for that, the theory that in solution an element is in a final, ideal and thoroughly combined condition. For the whole point of his theory is, that in solution an element is in this combined condition, that this combined condition is final so that no further chemical combination is possible, that an element having once given up its "thermochemical constant" passes from the free state into the "combined" state, that it does this on going into solution as an ion, and that any further changes cannot be one of combination, but must be that of a mere physical change of state.

I wish most strongly to take exception to this idea, that this state is one of complete combination, that an element having

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passed into it, has given out all the free chemical energy with which it is possessed, on the grounds that nowhere except in the case of these dilute solutions when the exception is explained by dissociation and independence of the ions from each other, do we see in the whole list of chemical compounds evidences that each element contributes a constant share of the heat of formation. An element as part of a solid compound is as much in combination as in the "ideal" condition in solution, and yet in entering their compound it may have undergone a change of energy greater or less than its "thermochemical constant." Consider the two following pairs of salts and their heats of formation:

NaCl	97562 cals.	$NaNO_3$.....	111420 cals.
$AgNO_3$	28692 "	AgCl	29410 "
	126254 cals.		140830 cals.

Here is a difference of 14576 calories, and yet the two pairs of salts consist of the same five elements in each case in what no one can deny is a most thoroughly combined condition.

The tables that Richards has prepared cannot be brought in as a support to his theory, as they are but another name for similar ones published by Ostwald under title of "Ionization Heats of the Elements." A short table appears in his *Lehrbuch der Allgemeinen Chemie* (1893, II, page 955), and a corrected table for about 20 kathions was published later in same year (*Zeits. physik Chem.*, II, page 501, 1893). These, as far as they are given, agree with Richards' table, but differ considerably from later values given by Ostwald himself (*Grundriss der Allgemeinen Chemie*, 1899, page 281). The basis of this table is the arbitrary value of zero given to the hydrogen ion, for the best determinations from electrochemical data give it a small value differing from zero by hardly more than probable experimental error. But however different the respective bases of the two tables are, the heat of formation of any salt given as the sum of the ionization heats of its component ions, should be the same in each table. In many instances the results given by the two tables differ considerably, yet Richards has omitted all reference to these previous tables and has given no grounds why his, differing as it does from Ostwald's, should supersede those which have long been considered authoritative.

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The main burden of proof of this theory is thrown by Richards on the explanation of neutralization on a purely physical basis. The well-known fact that when one equivalent of acid in dilute solution neutralizes an equivalent of base the heat liberated is independent of the acid or base and is equal to about 13700 calories. This fact, long considered remarkable, is usually explained by supposition that in the dilute solutions used the strong acid and strong base are almost completely dissociated into their respective ions. On mixing we would have a solution containing then, the kathion of the base the anion of the acid, hydroxyl and hydrogen ions. As $\overline{OH}$ and $\overset{+}{H}$ cannot exist in presence of each other to any appreciable extent, they combine to form undissociated water, while the other kathion and anion remain in their original condition. No other reaction then takes place except this combination of $\overset{+}{H}$ and $\overline{OH}$ and the heat of neutralization observed is no other than the heat of formation of water from the two ions. Ostwald (*Grundriss,* page 276) has carefully pointed out the danger of confusing the heat of formation of water under these circumstances with the heat of formation of water from the gaseous elements. For we are dealing in the one case with hydroxyl, not oxygen, and with hydrogen, not in gaseous state, but as ion. Each case is, however, an example of chemical action, though the heat liberated in the one is 68400 calories, in the other only 13700. Nevertheless, Richards denies this and objects strongly to the expression "heat of formation of water" when applied to the union of $\overline{OH}$ and $\overset{+}{H}$ ions. His explanation is as follows: "It is then a fundamental mistake to regard the neutralization as proceeding from an act of combination having the least analogy to a chemical act of combination, or of the neutralization heat having the slightest analogy to thermochemical heat of combination. For if the H and OH ions have once given out their thermochemical constants while entering into the state of combination as HCl and NaOH, they cannot give them out again, or any part of them in any further act of combination. The formation of liquid H_2O from $\overset{+}{H}$ and $\overline{OH}$ ions is therefore not a chemical act of combination and the neutralization heat is not in any sense then chemical heat of combination. The heat of

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neutralization, therefore, not resulting from chemical combination, must be physical in its nature," and further, "The act of neutralization is therefore merely the passage of $\overset{+}{H}$ and $\overline{OH}$ ions from the combined state in dilute solution, in which condition they exert osmotic pressure, into the combined state as liquid water, in which they exert practically no osmotic pressure. The change is exactly analogous to the change from the gaseous into the liquid condition, and is therefore the equivalent of the condensation of water vapor into the liquid state." In proof of this the following example from the work of Thompson is cited: $2\ NaOH\ 400\ H_2O + 2HCl\ 400\ H_2O = 2\ NaCl + 802\ H_2O +$ 27480 calories, which gives 13740 per equivalent.

Richards calculates the osmotic pressure of the NaOH and the HCl in their solution, since 400 H_2O have a volume of 7.2 liters, as 12.34 atmospheres. If on mixing no neutralization took place, the total osmotic pressure would remain unchanged and our total volume energy capable of doing osmotic work would be 12.34 x 14.4 liter-atmospheres. It will be necessary here to go into Richards' reasoning and calculation somewhat at length. "After neutralization," he states, "there remains only the osmotic pressure of the 2 NaCl in the 802 H_2O, which is 6.15 atmospheres, the osmotic pressure of the $\overline{OH}$ and $\overset{+}{H}$ together equal to 6.19 atmospheres disappearing because of the condensation of the water to the liquid state. The heat given out in this condensation is equal numerically to that necessary to convert 2 H_2O in the liquid state into vapor exerting in the gaseous state a pressure of 6.19 atmospheres." The heat of evaporation for one molecule or 18 parts water minus the outer work is shown to be 10110 calories. "The outer work, however, if the vapor exerts 6.19 atmosphere pressure is $6.19 \times 2T. = 6.19 \times 582 = 3590$ calories. The total heat of vaporization including the work necessary to give the vapor the requisite tension of 6.19 atmospheres is $10110 + 3590 = 13700$" an extremely close agreement with the 13740 observed heat. This agreement alone is used to substantiate the whole theory.

We may well ask how far this calculation, at least that for the outer work, is justified by the facts and by the well-known gas laws. The very expression in their general form $pv = RT$ shows

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that since the product of p and v is a constant the external work when a molecule of gas is formed and which is no more than an equivalent in calories for the volume energy pv, is a constant and absolutely independent of the gaseous pressure. Since one molecule of any gas at temperature of zero and under atmospheric pressure occupies a volume of 22.4 liters the expression $pv = RT$ can be solved for R by substituting values for p, v and T in the equation and we have

$$R = \frac{1033 \times 22400}{273} = 84736 \text{ gram centimeters}$$

$$1 \text{ calories} = 42660 \text{ grams}, \; R = \frac{84736}{42660} = 1.98 \text{ calories}$$

Since then 2T refers not only to a normal pressure of one atmosphere, but also to a normal volume, the external work cannot be given by ratio of pressure alone to normal pressure, but by ratio of product of pressure and volume to product of normal pressure and volume. The form of the calculation should be:

$$\frac{6.19 \times 14.4 \times 2T}{1 \times 22.4} = 4 \times 2T = 2328 \text{ calories}$$

This is for the formation of *two* H_2O, while the 10110 calories of latent heat to which it is added is that for *one* molecule. The above before addition must be divided by 2 and we have 1164 external work + 10110 calories latent heat = 11274 total heat neutralization referable to a physical basis. As the observed heat is 13740 calories I cannot see that Richards has sustained the theory that in the process of neutralization there is no act of chemical combination. For granting his premises that there is a full analogy between the condensation of water vapor and the formation of water in solution from its ions we come face to face with the evidence that this is totally against the experimental fact.

The question now arises as to how great a part, if any, of the heat of neutralization can be due to a physical change. We know that at least 2478 of the 13740 calories must be due anyway to chemical action, since that is the excess over the largest possible amount available to a physical cause. But how far are we right in drawing any strict analogy between the gases and a substance in dilute solution? In describing the state of a dissolved body we

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say that it exerts an osmotic pressure equal to the gaseous pressure it would exert were it really gaseous and occupying similar volume at the same temperature. But here the analogy stops. The molecule in solution is not gaseous. It is not moving through the solution as swiftly as a gaseous molecule would and its osmotic pressure is not due to any great degree to kinetic energy. In other words a molecule in solution, whether dissociated or not, though partaking of some of the properties of a gas, is not in a gaseous state. The dissociation of water into $\overline{OH}$ and $\overset{+}{H}$ ions cannot in any way be considered an actual change of state, or absorb a similar amount of energy in the same way a molecule of liquid water would in leaving actual liquid state and passing into the gaseous condition. This only applies to the 10110 calories latent heat. Here we are only doubtful of the analogy, but between the "outer" work in the two cases the analogy simply does not exist. If we vaporize a molecule of liquid, the volume of our system is increased, part of the heat applied to cause the vaporization is lost to our system, is used to push back the atmosphere. In the same way when a molecule water vapor condenses 2T or 582 calories of the observed effect owes its source to one external to the system. On the other hand, in the case of neutralization we have no actual changes in volume, merely a disappearance of osmotic pressure. There is no work done then upon our system, no external energy enters our system, and the 1164 calories osmotic work is not *outer* work, but owes its origin to energy changes within our solution. Between the $\overline{OH}$ and $\overset{+}{H}$ ions there exists a great amount of free potential energy. This must necessarily decrease as the two combine and it is to this change in the potential energy, which is no more than a chemical change, that the *whole* action is due.

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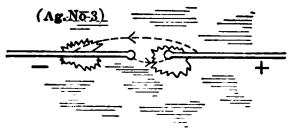
A communication before the New York Section of the American Electrochemical Society, New York, January 26, 1904, Vice-President Doremus in the Chair.

A STRANGE OBSERVATION.

By Ivar J. Moltkehansen.

Some years ago I made an observation, which, I think, may prove of some interest. I will describe it as I remember it, hoping that you may aid me in finding a satisfactory explanation. I had a strong silver nitrate solution and dipped into the solution two platinum wires as electrodes, and passed a current of high density through. After some time I found crystals of metallic silver forming on the cathode here (illustrating upon the blackboard), and apparently an equal quantity of silver crystals, white and crystalline, deposited on the anode. I called the attention of some fellow-students in the laboratory to the case, and we were greatly at a loss for an explanation. The reason for this deposition of



metallic silver on the anode could not be derived from the condition of the electrolyte, say by local electric currents due to a difference in concentration of the stratas of the silver nitrate solution; these electric forces are far too small to cause a silver deposition of a quantity as the one in question on the anode.

I happened to mention this observation at a recent meeting of the American Electrochemical Society to a couple of gentlemen, and one of them, a pioneer of electrochemistry, would explain this strange behavior of the silver nitrate solution from the high current density, and as he had often been aware, the poles of the electrodes are not at the end of such platinum wire, but further back. There is room then, if I understood him rightly, for the

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possibility of current of positive electricity running back toward the opposite end of the anode with a lower potential, and this point of the anode acting as a cathode to this branch current.

The fact that I observed two equally heavy white crystalline depositions at the same time formed on both electrodes in a silver nitrate solution is certain. Can any of the gentlemen throw some light on how it may have come about?

DISCUSSION.

MR. C. J. REED: I should like to ask Mr. Moltkehansen if he removed that deposit from the anode and analyzed it?

MR. IVAR J. MOLTKEHANSEN: I did not remove it and I did not analyze it.

MR. REED: Probably it was silver peroxide, which looks almost like silver and would necessarily form under those conditions.

MR. MOLTKEHANSEN: That might be the case, if silver peroxide could possibly be mistaken for silver, black for white; but to my knowledge silver peroxide is a black crystalline mass, and the crystals I observed on the anode silver were white.

MR. REED: Silver peroxide forms under those conditions very easily, and would resemble silver very closely, often having a white metallic crystalline appearance. It could not have been anything else.

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A paper, with specimens, read before the New York Section of the American Electrochemical Society, New York, January 26, 1904, Vice-President Doremus in the Chair.

EXHIBIT OF FERRO-METALS, MADE ELECTRICALLY, AND OF OTHER ELECTRIC FURNACE PRODUCTS.

By A. J. Rossi.

Certain refractory oxides cannot be reduced to any practical extent, if at all, at the temperatures prevailing in the blast furnace, and the progress of electric science in all its branches has alone rendered possible their reduction on an industrial basis. It may even be added that such metallic oxides as are now smelted readily and successfully in the blast furnace can, under certain conditions of cheapness of current, price of raw material, and favorable location be treated electrically as economically as by the ordinary metallurgical methods. In this way steel, made electrically, is spoken of now as an industrial possibility, and that even pig iron for limited production to supply local demands, in specially advantageous circumstances, can also be smelted electrically with profit. It is not for us to discuss this question here, we do not want to be understood to say that electric processes will everywhere and always replace other metallurgical methods. We desire only to state that which is incontestable, viz., that what was considered as a dream a few years ago as to practical applications of electricity has become, in many cases, a reality which furnishes us sufficient reason to hope for or foresee further developments.

Among refractory metallic oxides, titanium and vanadium have proven the most difficult to reduce, owing to their impressibility as metals and even as ferro alloys. Next to them come tungsten and molybdenum, and, to a certain extent, ferro silicon (considered as a ferro metal, though silicon is a metalloid).

The reduction of oxides by electricity is secured in exactly the same manner, whatever they may be, and, for this reason the description of the methods followed with one can be said to apply to all the others. Ferro metals, as a rule, are more fusible than the metals themselves, and the presence of carbon in the metal, *cæteris paribus,* has also an influence on the fusibility; but this

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must be understood to be merely comparative as certain ferros or metals containing carbon are really but little *fusible,* according to our ordinary interpretation of the word.

Two methods can be resorted to to obtain the metal or the ferro from the oxides. If the oxides which form the first materials are associated with oxides of iron, which is most frequently the case, according to the percentage of the latter present, a metal containing but little iron, or what may be called more properly a ferro metal containing a lesser or greater percentage of the metal, is obtained.

If the presence of carbon in the product is not considered objectionable, carbon is used as a reducing agent. The oxide in powder, being charged with the proper amount of powdered carbon in some form; in an electric furnace, for instance, one of the arc type (essentially consisting in a cavity in a masonry of graphite, connected with one of the bus bars of the generator and of a carbon pencil connected with the other, and which can be moved vertically in the cavity-forming crucible), the current is turned on. The oxide is reduced to the metallic state and the metal or its ferro, as the case may be, containing more or less carbon either in a combined state or as graphite is obtained. This carbon can be removed, in part at least, by a subsequent treatment in the electric furnace, but if very small quantities of this element are not admitted for special applications, the reduction of the refractory oxide can be and is secured by another metal, the heat of combination with oxygen of which is greater, at the temperature at which the operation is conducted, than that of the oxides to be reduced. Aluminum having one of the greatest of heats of combination known, is the metal which is resorted to, and here again we have a metallurgical operation, inadmissible industrially a few years ago, which has been rendered possible by the development of electricity, which has furnished the metal aluminum at a reasonable rate. This power of aluminum to cause a reduction of metallic oxides has been well known for more than fifty years, but could only be practiced in the laboratory on a very small quantity of material as an experiment, the *modus operandi* rendering the reaction violent and even dangerous, the mixture of powdered aluminum and powdered metal being charged in a crucible heated externally. It was due to Dr. Hans Goldschmidt to render this use of

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aluminum in a fine state of division practicable by a very ingenious method which implies other important applications. It is too well known for us to dwell upon it, as it has been even illustrated here by Dr. Goldschmidt himself in a lecture delivered recently at Columbia University.

One drawback to this method, for this special application to the reduction of oxides, is the cost of the aluminum in powder, as compared to that of the metal as ordinarily supplied to the trade (being double or more than double). We have proposed and practiced another method in which we use the aluminum in ingots, waffles or scrap (previously melted in an electric furnace), as a reducing agent. The aluminum, as obtained in ingots or the like, being charged in the furnace, the current is turned on, the metal melts at once, and the oxides to be reduced are shoveled in this bath of aluminum. The apparatus can be controlled by diminishing or altogether stopping the current, which can be turned on again to maintain the metal or ferro metal in a molten state, and even purify it from any excess of aluminum or any other element considered objectionable by means of proper additions before casting.

The specimens exhibited to you as a product of the application of this method include ferro titanium, containing from 10 to 25 per cent., 35, 45 and 55 per cent. titanium, and only a few hundredths to a few tenths of 1 per cent. of carbon.

The alumina resulting from the reduction of the metallic oxides formed a slag over the metallic bath, this slag consisting essentially of alumina (65 to 85 per cent.), combined with the earthy bases of the ores used and carrying a little titanic acid and silica. Specimens of this slag, which occasionally crystallized beautifully, are exhibited to you as "alumina slag." It is extremely hard, scratching glass and quartz like corundum.

By substituting for certain ferruginous ores, tungsten, chromic, molybdic, ores concentrates containing some oxide of iron we have obtained in the same manner: "*ferro-tungsten,* at 76 to 78 per cent. tungsten;" "*ferro-chrome,* at 65 to 68 per cent. chromium;" "*ferro-molybdenum,*" of which we show you some specimens.

We exhibit to you also the products of the electrical reduction of carbon on some metallic oxides, such as *ferro-titanium* from 10 to 20 and 30 per cent. titanium, *ferro-chrome* of about 65 per

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cent., both containing carbon from 7 to 9 per cent., more or less, and *ferro-silicon,* containing some 30 per cent. silicon; also, ferro-manganese, of 50 to 85 per cent. and spiegel of 25 per cent. These were smelted *electrically* from ores in which their physical state excluded their use in the blast furnace, and which can be had for the digging, like peat.

Whenever the metallic oxides to be reduced are associated with oxides of iron, a certain quantity of aluminum has to be added for the reduction of the latter, and, for ferro-titanium, for instance, unless rutile be used, there is on this score a certain expense for aluminum. When rutile is used alone, the addition of a bath of metallic iron in the furnace gives ferros of any percentage, and this addition considerably facilitates the operation; the same may be said of titaniferous ores too high in titanium if a moderate percentage is desired. The cost of rutile, however, enters as an important factor, and whenever its price has to be considered, we have used for reduction by aluminum what may be called an *artificial rutile,* obtained by adding carbon in quantity just sufficient to reduce the oxides of iron present in the ore, and not the titanic acid, adding a little lime as flux. By this operation a valuable pig iron is the product, the rutile passing in the slag which does not contain any more iron than an ordinary blast-furnace slag and which forms as a by-product, an *igneous concentrate,* of which the price is nominal, and which forms an excellent material for cheaper reduction by aluminum than the rutile. We exhibit to you, *first,* the ore used, containing some 15 to 16 per cent. iron, 80 per cent. oxide of iron and 4 per cent. of gangue, and others containing 38 per cent. titanic acid and 35 per cent. of metallic iron, 50 per cent. oxide of iron; *second,* the pig iron obtained from it, by reduction with carbon. It contained only 0.03 to 0.04 titanium; *third,* the igneous concentrate containing some 70 to 75 per cent. or more of titanic acid with but 2 or 3 per cent. oxide of iron; *fourth,* the ferro-titanium obtained from the concentrates by aluminum and containing some 10 per cent. titanium and no carbon; *fifth,* the aluminum slag resulting from the preceding operation, containing mostly lime and magnesia.

The carbon alloys, containing titanium, were used by us to treat cast iron, of which it increases the strength considerably (30 per cent. or more), and the alloys free from carbon, were

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used by us to season steel. This addition, in a general way, appears to considerably increase the elasticity of steel high in carbon, as shown by the remarkable increase of the elastic limit, and the high contraction of area of the section. Titanium acts very much like vanadium, as far as experiments have been carried with the latter, and in this respect it is interesting to note that vanadium and titanium have almost the same atomic weight: 47.7 T./50.8 for vanadium, the same specific gravity: (4.90 T/5.20 vanadium), and, which is curious, vanadic acid is almost invariably found in small quantities in titaniferous iron ores, and which is still more worthy of notice, it appears from analyses that the ratio of vanadic acid to titanic acid in titaniferous iron ores from the most different kinds of ore, is practically constant 28 titanic acid to 1 vanadic acid. Both metals are quite infusible and their ferros contain above 25 to 30 per cent. of metal difficult of use on this score. By adding to the aluminum bath some copper or oxide of copper, before charging rutile (titanic oxide) or even concentrate, we have obtained some cupra-titanium, containing from 10 to 14 per cent. titanium which we exhibit and with which we have made alloys of copper and titaniums containing from ½, 1, 2 and 5 per cent. copper, of which we show you specimens.

As curious products of the electric furnace we exhibit to you alumina slags, in a slaty form, in a beautifully crystallized form, as also casual products, such as nitride and cyanonitride of titanium, gluconide of titanium, crystals of alloys, nearly ¾-inch square and graphitic products.

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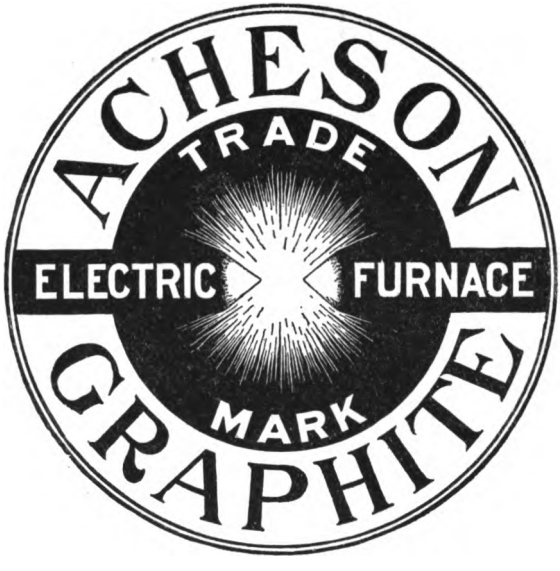

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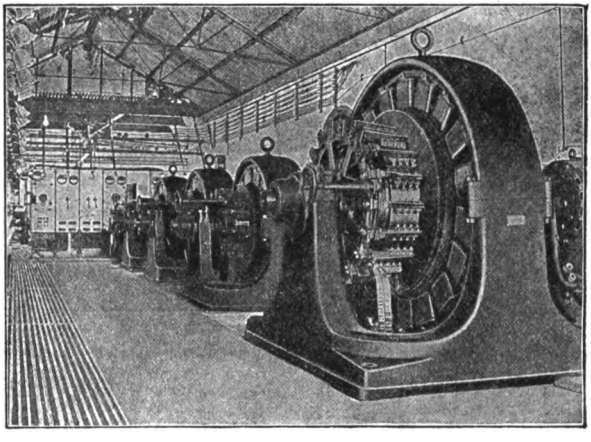

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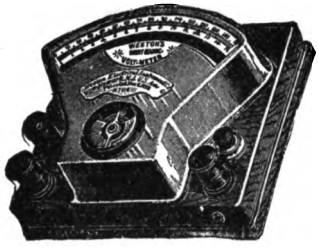

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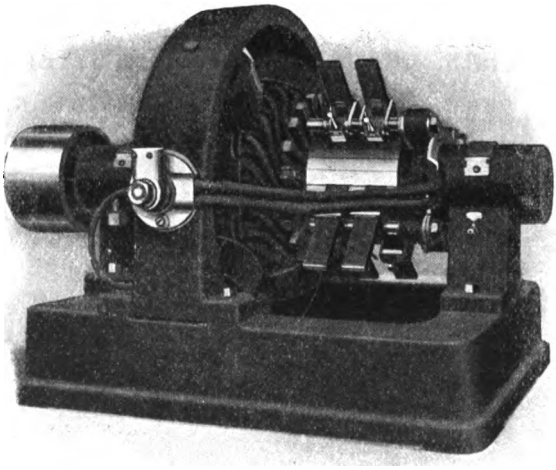

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